Carbon Nanotubes—A Status Report

by Shekhar Subramoney

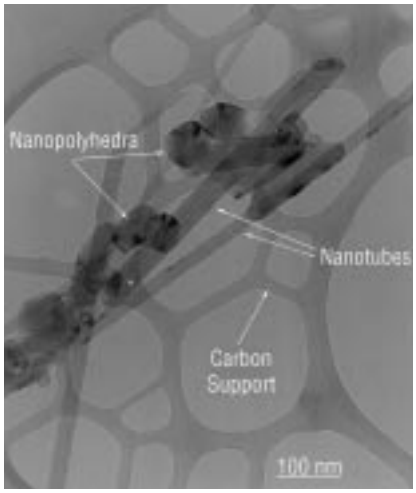

FIG. 1. Bright-field TEM image of arc processed carbon nanotubes, multi-walled nanopolyhedral particles are present as well.

To begin with, one could ask "Why are we so interested in nanometer scale hollow tubes of carbon with typical aspect ratios of about 100?" From a materials science perspective, the oil crisis of the 1970s provided a major impetus for the development of materials that combined light weight with exceptional mechanical properties. There was a major shift from metal based materials to the development of ceramics, polymers, and, of course, composite materials. Conventional fiber-based composite materials use reinforcements such as fiber glass, Kevlar® aramid fibers, or carbon fibers (either polyacrylonitrile (PAN) based or pitch based). Glass fibers and chips are available at attractive enough costs to make them viable candidates for large scale commercial applications such as automotive panels. At present, however, this is not the situation with carbon fibers. The relatively higher cost of carbon fibers currently makes them suitable only for specific military, aerospace, or sporting goods applications such as tennis racquets or golf clubs.

In the early 1980s, based on assumptions that composite reinforcements below the critical Griffith crack size would enhance mechanical properties such as strength, significant research efforts were directed toward the development of what are known as "molecular composites."[1] The intuition was that nanometer scale reinforcements would not only satisfy the Griffith criterion, but would also be less fraught with defects, due to their dimensions, compared to their micrometer-sized counterparts. Carbon nanofibers were conceptualized as ideal candidates for such molecular composites. Interestingly enough, the existence of nanoscale carbon filaments was already known for about four decades at that time and they were viewed more as a hindrance than as a beneficial material. They were found, mostly by accident, inside furnaces and reactors containing hydrocarbon gases or carbon monoxide[2] and their formation was attributed to the catalytic action of several metals or their oxides or carbides.[3] However, due to the relatively low temperatures inside the reactors (such as several hundreds of degrees Centigrade), these nanofilaments were poorly ordered and would typically suffer from relatively poor mechanical properties.

Buckyballs and Buckytubes

In 1985, the serendipitous discovery of the third form of ordered carbon (after diamond and graphite) known as buckminsterfullerenes[4] (or buckyballs) created a tremendous amount of excitement in the scientific community. One of the basic concepts realized at that time was that an infinite number of closed ordered carbon structures could be produced by the introduction of 12 pentagons into the hexagonal network. In fact, in 1991 it was conceptualized by researchers at the Naval Research Laboratory that tubular structures analogous to the buckyballs could have electronic properties more similar to metals than graphite. The synthesis of buckyballs in larger quantities by the arc-discharge process[5] subsequently lead to Sumio Iijima's work of discovering what we know as multi-walled carbon nanotubes (MWNT).[6] Interestingly enough, the theoretical work out of the Naval Research Laboratory[7] (which had been originally deemed as being too speculative as nanotubes had not been experimentally synthesized when it was written) was only accepted for publication following Iijima's discovery! Figures 1 and 2 are transmission electron micrographs (TEM) of multi-walled carbon nanotubes produced by the arc-discharge process[6] and by a vapor growth process with nanometer scale transition metal catalyst particles, respectively. Comparison of these images clearly illustrates that the tubes produced by the arc-discharge process are significantly defect-free compared to the vapor grown nanofilaments—which appear substantially curled up due to a large number of lattice defects along their length.

Unlike conventional fullerenes, which form in the vapor phase, MWNTs observed by Iijima and subsequently by a number of researchers the world over occur in the "boule" that grows on the face of the negative electrode (cathode) during the arc-discharge process. These MWNTs, which typically had aspect ratios close to 100, were significantly more graphitized (due to fact that the temperature in the arc plasma is anywhere between 3500 and 5000°C) than their vapor grown counterparts and closed at each end by pentagons similar to the buckyballs. Iijima also demonstrated that the individual tubes comprising these MWNTs were helical with varying degrees of helicity. A very large number of scientific publications in the 1990s have

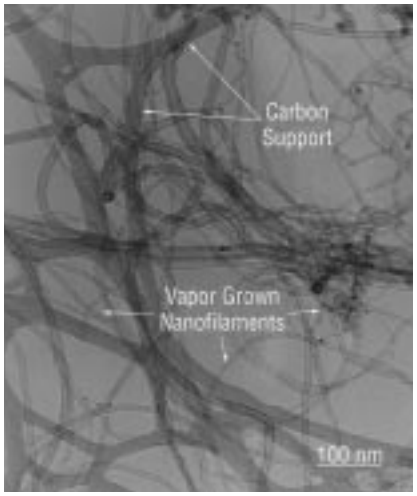

FIG. 2. Bright-field TEM image of vapor phase grown carbon nanofilaments.

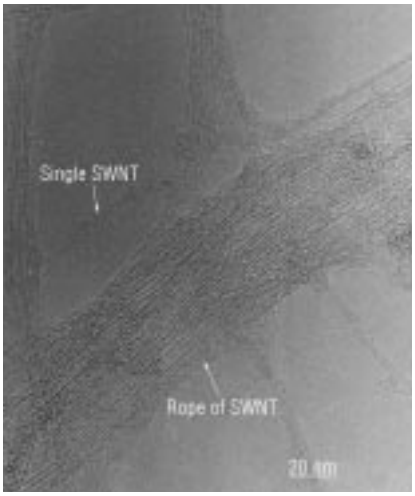

FIG. 3. High resolution TEM image of single-walled carbon nanotubes grown by the arc process.

addressed the growth mechanism of these novel structures, which by itself is a complex and fascinating topic. One of the concerns about the arc discharge process was the quantity of nanotubes produced; they occur in conjunction with other forms of carbon such as equiaxed multi-walled polyhedral particles, graphitic sheets, and amorphous carbon. Subsequent research[8] clearly established relationships between the quantity of nanotubes formed and process variables such as arc-discharge current, inert gas pressure within the chamber, and electrode cooling rates. While this was a step in the right direction, the formation of the other species of carbon mentioned earlier could not be entirely eliminated during the arc-discharge process. This problem lead to several investigators examining methods to purify the MWNTs using various techniques. One of the more successful techniques employed was the preferential oxidation of the other forms of carbon to leave behind a sample that was composed only of nanotubes.[9] The major drawback of the oxidation technique, however, is that more than 99% of the "boule" material is consumed before one obtains a sample of pure MWNTs (almost a definite no-no for any possible commercial process).

The excitement of producing pure MWNTs by any technique was eclipsed in 1993 by the simultaneous discoveries at NEC (Japan) and at IBM (USA) of large quantities of single walled carbon nanotubes (SWNTs).[10] These fascinating structures grow as bundles in the vapor phase of the arc discharge process when small amounts of transition metals were incorporated into the graphitic anode, with each SWNT approximately 1.2 nm in diameter. A typical high resolution electron micrograph of ropes of SWNTs processed in the vapor phase of an arc-discharge is illustrated in Fig. 3. Considering that most of the theoretical work to date had addressed single-walled tubes, these discoveries were extremely significant indeed. Compared to MWNTs, one of the most significant features of SWNTs is the uniformity of size and the relative lack of any defects in the latter. While the role of the transition metal catalysts and the formation mechanism of SWNTs are still subjects of scientific debate, subsequent research proved that combinations rather than single transition metals were more effective in catalyzing their growth.[11] And, unlike their multi-walled counterparts, methods to produce SWNTs in significantly large quantities developed rather quickly. One of the biggest breakthroughs in this front was the use of a double laser vaporization technique with mixtures of transition metal catalysts rather than an arc-discharge process. This work at Rice University[12] resulted in the production of fairly large quantities (at least at levels commensurate with what was needed for further studies) of SWNTs with relatively small concentrations of associated products such as amorphous carbon. Electrical resistivity measurements on the ropes of SWNTs by a four probe technique indicated that they were the most highly conductive carbon fibers ever measured with resistivities at least an order of magnitude lower than the MWNTs. This property, in combination with their ultrafine dimensions, would make them ideal quantum wires, where currents would increase or decrease in step-wise modes rather than in a continuous mode—something very similar to fiber optics!

Large Scale Processes for SWNTs and MWNTs

By the mid-1990s, it was fairly evident to the research community that carbon nanotubes were fascinating, novel materials with unique properties that would make them extremely attractive for specific applications. However, three criteria needed to be addressed to make them viable for commercial applications: mass production at acceptable costs or production at levels commensurate with specific applications; production of pure nanotubes with little or no side products; and demonstration of specific applications where nanotubes perform better than any other material. To a large extent, it was also very apparent that these three issues were interlinked. A number of academic and industrial research groups the world over are currently working on all of the above issues.

At present, large scale synthesis of SWNTs appears to be a high priority. While the Rice University work[12] demonstrated that yields in the 70 to 90% range can be achieved using catalysts composed of transition metal mixtures, the use of transition metal/rare earth metal mixtures in an electric arc appears to be even more promising in terms of yield as well as costs.[13] The structure of the tubes obtained by the electric arc method using transition metal/rare earth metal co-catalysts was found to be similar to the laser produced tubes as determined by scanning and transmission electron microscopy, wide angle X-ray diffraction, and Raman spectroscopy. It was also demonstrated that gram quantities of SWNTs could be produced by this method, and the authors claim that it is a relatively inexpensive technique that can be easily scaled up. The mechanism by which SWNTs form is not yet established, but it appears that they form under non-equilibrium conditions in which carbon condenses from the vapor phase in which parameters such as temperature and temperature gradients play important roles.

While techniques such as arc-discharge and laser evaporation have been demonstrated as being successful for producing gram quantities of carbon nanotubes, they are still quite a ways

from the kilogram range of quantities one would need for any feasible commercial application. Several researchers are currently re-examining critical aspects of an old fashioned technique, namely, the decomposition of hydrocarbons in the presence of catalysts to produce both SWNTs and MWNTs in preferred arrays or in large quantities to make them directly suitable for applications. In these chemical vapor deposition (CVD) processes, the catalyst composition, the nature of the catalyst metal/support interaction, and the reaction kinetics appear to be important parameters that need to be thoroughly understood for large scale SWNT synthesis.[14] In the case of SWNTs, it is also possible to use CVD techniques to synthesize SWNTs in patterned arrays.[15] This type of synthesis technique should enable the fabrication of devices where the nanotubes offer specific advantages in performance over other materials, as will be discussed later in this paper.

Patterned growth of arrays of nanotubes is not confined to SWNTs. The aligned growth of multi-walled tubes, as well as individual freestanding tubes in an array, has been discussed in recent publications by Ren and his colleagues.[16, 17] This is also achieved by the decomposition of hydrocarbons over supported transition metal catalysts by the process known as plasma enhanced hot filament chemical vapor deposition (PE-HF-CVD). What was extremely interesting in this process was that the thickness of the nickel layer on the glass support appeared to be an important parameter in controlling the diameter of the nanotubes produced in the array. The other interesting aspect was the presence of nickel nanoparticles on the tip of each tube, asserting the catalytic role played by nickel in their formation. A relatively mild etching treatment by nitric acid was also successful in removing these nickel caps, resulting in an array of almost pure MWNTs without any of the associated carbon nanostructures that were discussed previously. As with SWNTs, such patterned growth of MWNTs should enable the direct fabrication of devices that would exploit the specific properties of nanotubes.

Potential Applications

During the course of the decade, the novel form of carbons referred to as nanotubes were discovered as a by-product of fullerenes. Subsequent research (both theoretical and experimental) has shown that the nanotubes would have superior mechanical and electrical properties that would make them suitable for many unique applications. As conjectured by Yakobson and Smalley,[18] a diverse portfolio of applications, ranging from molecular composites to microelectronics to nanoprobes for chemical and/or biological applications to storage devices for hydrogen, might be achieved with nanotubes. Some fascinating applications have already been demonstrated at the prototype stage using carbon nanotubes, as will be discussed later in this section.

As discussed earlier, the processing of large quantities of both SWNs and MWNTs (specifically in patterned arrays) using modified CVD techniques opens the possibility of using nanotubes in a large number of microelectronic applications. Even when SWNTs are formed as large tangled ropes where individual ropes are composed of hundreds of SWNTs, it has been demonstrated using simple chemical means that it is possible to convert this messy structure into short, open-ended pipes which behave like individual macromolecules.[19] The cutting of nanotubes into short sections would in turn permit a variety of manipulations for subsequent applications. It is also possible that once the tubes are opened, a whole new class of chemical reactions may be achievable.

The growth of patterned arrays of nanotubes sometimes results in tubes bridging some of the supporting metallic islands,[15] which in turn may enable the development of ultrafine electrical interconnects for specific devices. Whether these forms of interconnects can be created on a deliberate basis is a question that has not yet been answered. However, the use of nanotubes as ultrafine probes for scanning probe microscopy has already been demonstrated.[20] In this work, the authors demonstrated that MWNTs constituted well defined tips for scanning probe microscopy when they were attached to the silicon cantilevers of conventional atomic force microscopes (AFM). Due to their flexibility, the MWNT tips were found to be resistant to damage from tip crashes, while their ultrafine diameters enabled them to probe recesses in the specimen surfaces more effectively than conventional silicon tips. The excellent electrical conductivity of nanotubes could also be potentially exploited to utilize them for scanning tunneling microscopy (STM). The authors, however, caution that a significant amount of development is needed before the use of nanotubes as tips for scanning probe microscopes on a commercial basis.

FIG. 4. Carbon nanotube-based 4.5-inch field emission display unit. (Reprinted with permission from Dr. Wong Bong Choi and Samsung Advanced Institute of Technology.)

The use of nanotubes, specifically SWNTs, as storage devices for clean fuels (such as hydrogen in hydrogen-based fuel cells) is a topic that is currently attracting a significant amount of interest. Temperature-programmed desorption studies using SWNTs[21] appears to demonstrate that hydrogen will condense inside the SWNT capillaries, with typical hydrogen uptake ranging from 5 to 10% by weight at -140°C and pressures of 300 torr. In recent experiments where the nanotubes were doped with alkaline metals, it appeared that hydrogen uptake increased to about 20% at temperatures ranging from 200 to 400°C at ambient pressures.[22] Concerns such as whether the hydrogen is incorporated in the molecular or protonated form, and whether the adsorbed hydrogen can be released for use as fuel under conventional conditions have yet to be addressed.

One of the niftiest applications that appears to be developing using carbon nanotubes is field emitting displays that are significantly brighter than either cathode ray tubes or Spindt tip based displays. The Samsung Advanced Institute of Technology in Suwon, Korea has recently unveiled a matrix-addressable 4.5-inch diode-based flat panel display prototype where the cathode consists of ropes of SWNTs. Typical rope densities in this prototype display range between 3 and 5 ropes per square micrometer of cathode surface. Figure 4 is a photograph of this prototype under emission conditions, with phosphors for red, blue, and green colors deposited in individual

strips on the anode, and individual pixel size is 300 µm X 300 µm. This prototype display can be turned on low voltages (less than 1V/µm), and the green phosphor, which is considerably brighter than either the red or the blue, has a brightness on the order of 1800 cd/m^2 at 4V/µm. This prototype also has remarkable current fluctuation characteristics and appears to have a fairly long display life. The cost of the unit is mostly dependent on the cost of the SWNTs and would be easily scalable to larger sizes and quantities. However, one of the major challenges for the display industry is to develop triode-based displays where individual pixels can be addressed individually with emission and brightness characteristics similar to what has been demonstrated to date.

In summary, the 1990s has been a decade that has witnessed the birth of a novel class of materials that we refer to as carbon nanotubes. These new materials have evidently sparked a considerable amount of excitement in chemists, physicists, and materials scientists the world over. During the course of a very short decade, we have gone from the discovery to seeking methods to produce these materials in commercial quantities, to discovering applications where nanotubes clearly outperform the incumbents. If the 1990s are any indication, the 2000s should be a very exciting time for scientists and engineers working with carbon nanotubes. ■

References

1. P. Calvert, *Nature,* **357**, 365 (1991).
2. W. R. Davis, R. J. Slawson, and G. R. Rigby, *Nature,* **171**, 756 (1953).
3. N. M. Rodriguez, *J. Mater. Res.*, **8**, 3233 (1993).
4. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature,* **318**, 162 (1985).
5. W. Kratschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature,* **347**, 354 (1990).
6. S. Iijima, *Nature,* **354**, 56 (1991).
7. J. W. Mintmire, B. I. Dunlap, C. T. White, *Phys. Rev. Lett.*, **68**, 631 (1992).
8. T. W. Ebbesen and P. M. Ajayan, *Nature,* **358**, 220 (1992).
9. T. W. Ebbesen, P. M. Ajayan, H. Hiura, and K. Tanigaki, *Nature,* **367**, 519 (1994).
10. S. Iijima and T. Ichihashi, *Nature,* **363** (1993); D. S. Bethune, C. H. Kiang, M. S. de Vries, G. Gorman, R. Savoy, J. Vasquez, and R. Beyers, *Nature,* **363**, 605 (1993).
11. S. Seraphin, *J. Electrochem. Soc.*, **142**, 290 (1995).
12. A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer, and R. E. Smalley, *Science,* **273**, 483 (1996).
13. C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapelle, S. Lefrant, P. Denlard, R. Lee, and J. E. Fischer, *Nature,* **388**, 756 (1997).
14. A. M. Cassell, J. A. Raymakers, J. Kong, and H. Dai, *J. Phys. Chem. B,* **103**, 6484 (1999).
15. J. Kong, H. T. Soh, A. M. Cassell, C. F. Quate, and H. Dai, *Nature,* **395**, 878 (1998).
16. Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegel, and P. N. Provencio, *Science,* **282**, 1105 (1998).
17. Z. F. Ren, Z. P. Huang, D. Z. Wang, J. G. Wen, J. W. Xu, J. H. Wang, L. E. Calvet, J. Chen, J. F. Clemic, and M. A. Reed, *Appl. Phys. Lett.*, **75**, 1086 **(**1999).
18. B. I. Yakobson and R. E. Smalley, *American Scientist*, **85**, 324 (1997).
19. J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y. -S. Shon, T. R. Lee, D. T. Colbert, and R. E. Smalley, *Science,* **280**, 1253 (1998).
20. H. Dai, J. H. Hafner, A. G. Rinzler, D. T. Colbert, and R. E. Smalley, *Nature,* **384**, 147 (1996).
21. A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, and M. J. Heben, *Nature,* **386**, 377 (1997).
22. P. Chen, X. Wu, J. Lin, and K. L. Tan, *Science,* **285**, 91 (1999).

About the Author

Shekhar Subramoney *is a Senior Research Chemist with the Central Research and Development division of the DuPont Company in Wilmington, Delaware. His primary assignment at the DuPont Company is the analysis of materials ranging from catalysts to polymers to inorganic particulates through the use of electron microscopy and associated techniques. Dr. Subramoney also conducts research on novel forms of carbons and has published extensively in this field. He has organized the Nanotubes and Nanostructured Materials session at the annual meetings of The Electrochemical Society since 1993 and also serves as Treasurer of the Fullerenes Group.*