WTEC Panel Report on

INTERNATIONAL ASSESSMENT OF RESEARCH AND DEVELOPMENT OF CARBON NANOTUBE MANUFACTURING AND APPLICATIONS

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WTEC PANEL FOR R&D OF CARBON NANOTUBE MANUFACTURING AND APPLICATIONS

Sponsored by the National Science Foundation, the Office of Naval Research, the National Institute of Biomedical Imaging and Bioengineering, and the National Institute of Standards and Technology.

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WTEC

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FINAL REPORT

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Abstract

This WTEC study focuses on the manufacturing and applications of carbon nanotubes (CNTs) to identify recent progress in understanding the commercial potential of CNTs as viewed by academic, industrial, and government research facilities around the world. CNT manufacturing methods and equipment, processing and separation techniques, characterization procedures, and opportunities for international collaboration are highlighted in this study. These issues are also discussed in the context of leading electronic, optical, and mechanical applications of CNTs ranging from transistors to structural composites.

CNTs can be produced by many methods, and depending on the diameter, one can obtain either single-walled CNTs (SWCNTs) or multi-walled CNTs (MWCNTs). The current capacity for the production of MWCNTs far exceeds that of SWCNTs. SWCNTs are much more expensive and difficult to manufacture than MWCNTs, and there is not yet a distinct large-scale market for SWCNTs, which is needed to drive down the production cost. For both types of CNTs, Asia's production capacity is two to three times higher than that estimated for North America and Europe combined; Japan is the prominent leader in the production of MWCNTs. Use of CNTs in lithium-ion battery electrodes is the current driving force of ton-scale MWCNT production in Japan. CNT-replacement products for indium tin oxide (ITO) and field emission devices (FEDs) are driving increased production of SWCNTs, whereas applications using transistors require precise control over CNT diameter and conductivity, which is farther from commercial realization. When the cost of bulk SWCNTs decreases significantly, applications in electromagnetic shielding (EMI) and electrostatic discharge (ESD) protection can be expected, and SWCNTs will replace MWCNTs in conductive plastics. Currently, owing to challenges in CNT functionalization and dispersion, CNTs can only achieve modest enhancements in mechanical properties of materials. While sporting goods with CNT reinforcement are beginning to appear on the market, improved processing techniques along with manufacturing techniques for long and aligned CNTs (e.g., yarns and aligned arrays) are needed to realize CNT-based materials that provide compelling advantages over existing fiber composites in lightweight structures.

World Technology Evaluation Center, Inc. (WTEC)

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FOREWORD

> We have come to know that our ability to survive and grow as a nation to a very large degree depends upon our scientific progress. Moreover, it is not enough simply to keep abreast of the rest of the world in scientific matters. We must maintain our leadership.[1]

President Harry Truman spoke those words in 1950, in the aftermath of World War II and in the midst of the Cold War. Indeed, the scientific and engineering leadership of the United States and its allies in the twentieth century played key roles in the successful outcomes of both World War II and the Cold War, sparing the world the twin horrors of fascism and totalitarian communism and fueling the economic prosperity that followed. Today, as the United States and its allies once again find themselves at war, President Truman's words ring as true as they did a half-century ago. The goal set out in the Truman Administration of maintaining leadership in science has remained the policy of the U.S. Government to this day: Dr. John Marburger, the Director of the Office of Science and Technology (OSTP) in the Executive Office of the President made remarks to that effect during his confirmation hearings in October 2001.[2]

The United States needs metrics for measuring its success in meeting this goal of maintaining leadership in science and technology. That is one of the reasons that the National Science Foundation (NSF) and many other agencies of the U.S. Government have supported the World Technology Evaluation Center (WTEC) and its predecessor programs for the past 20 years. While other programs have attempted to measure the international competitiveness of U.S. research by comparing funding amounts, publication statistics, or patent activity, WTEC has been the most significant public domain effort in the U.S. Government to use peer review to evaluate the status of U.S. efforts in comparison to those abroad. Since 1983, WTEC has conducted over 60 such assessments in a wide variety of fields, from advanced computing, to nanoscience and technology, to biotechnology.

The results have been extremely useful to NSF and other agencies in evaluating ongoing research programs, and in setting objectives for the future. WTEC studies also have been important in establishing new lines of communication and identifying opportunities for cooperation between U.S. researchers and their colleagues abroad, thus helping to accelerate the progress of science and technology generally within the international community. WTEC is an excellent example of cooperation and coordination among the many agencies of the U.S. Government that are involved in funding research and development: almost every WTEC study has been supported by a coalition of agencies with interests related to the particular subject at hand.

As President Truman said over 50 years ago, our very survival depends upon continued leadership in science and technology. WTEC plays a key role in determining whether the United States is meeting that challenge, and in promoting that leadership.

Michael Reischman
Deputy Assistant Director for Engineering
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[1] Remarks by the President on May 10, 1950, on the occasion of the signing of the law that founded the National Science Foundation. *Public Papers of the Presidents* 120: 338.

[2] http://www.ostp.gov/html/01_1012.html.

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EXECUTIVE SUMMARY

Peter C. Eklund

INTRODUCTION AND BACKGROUND

In March 2006, the National Science Foundation (NSF), the Office of Naval Research (ONR), the National Institute of Standards and Technology (NIST), and the National Institute of Biomedical Imaging and Bioengineering (NIBIB) of the National Institutes of Health (NIH) requested the World Technology Evaluation Center (WTEC) to make an international assessment of the manufacturing and applications of carbon nanotubes (CNTs). The purpose was to gather and disseminate information on the worldwide status and trends in CNT manufacturing and applications. A panel of eight experts from universities and industry was organized and chaired by Professor Peter Eklund from Pennsylvania State University. The panel first held a North American Workshop on June 2, 2006, to gather information on CNT activity in Canada and the United States. The WTEC CNT Panel then traveled in the fall to Korea, China, and Japan to survey the primary activity in Asia.

Carbon nanotubes appear to have been discovered in the late 1970s by Professor Morinobu Endo during his experiments to produce micron diameter carbon fibers (Oberlin 1976). During this time he published several transmission electron microscope (TEM) images showing very small diameter carbon filaments, which he described as a tube formed by rolling up a plane of carbon atoms as found in graphite. Surprisingly, Endo's discovery passed largely unnoticed until very recently. In 1991, some fifteen years later, articles such as "Helical Microtubules of Graphitic Carbon," published in *Nature* by Iijima (1991), demonstrated that CNTs could be produced in an arc discharge between carbon electrodes in He gas. Small quantities of CNTs then became available for study. Iijima and co-workers used this material and modern transmission electron microscopes to provide evidence for the structure of CNTs that we know today. They found that the CNTs could be open-ended, or closed with a hemispherical cap resembling half of a fullerene molecule. The work of Iijima and his coworkers resulted in a "feeding frenzy" by researchers worldwide to learn how to produce CNTs in larger quantities and of better quality. The race was on to elucidate their properties and to develop new technology taking advantage of the unique properties of these atomic filaments.

Endo, in his early review of vapor-phase-grown carbon fibers (VPCF), also reminds us that he has observed a hollow tube, linearly extended with parallel carbon layer faces near the fiber core.(Endo 1988). This appears to be the observation of multi-walled carbon nanotubes at the center of the fiber. This work by Endo also contains several relatively unknown and very early references to the growth of carbon whiskers by R.J. Bacon and the earliest carbon fibers reported in 1890. The mass- produced MWCNTs (Japan) today are strongly related to the VPGCF developed by Professor Endo. In fact they call it the "Endo-process", out of respect for his early work and patents. In fact, these MWCNTs are really small diameter VPGCFs subsequently subjected to a high temperature heat treatment (HTT) in an inert atmosphere. This HTT drives the structure into a more organized set of concentric tubes of carbon. The manufacture of these MWCNTs is described later in the report.

The covalent carbon-carbon bonds within a CNT are among the strongest known. In addition, CNTs are remarkably compliant, i.e., they are able to make sharp bends without fracture. It is therefore expected that CNTs could be incorporated in revolutionary lightweight composites. To perfect these CNT composites, challenges exist in their dispersion into the host and also in developing strong, covalent coupling of the CNT to the host medium.

The electronic structure of a CNT is also remarkable. The nature of the electrical conductivity along the tube axis was predicted theoretically to depend uniquely on the integers (n, m). These predictions were soon confirmed by experiment. Energy band theory predicted that two-thirds of all possible CNTs would be

semiconducting with a gap $E_g \sim 0.6$ eV/d, where d is the diameter of the tube (Dresselhaus, Dresselhaus, and Avouris 2001). The remaining one-third of all CNTs should be metallic due to band overlap. Quite remarkably, several research groups soon found ballistic transport in CNTs at cryogenic temperatures, indicating that it was possible for electrons to pass distances ~100 nm down the tube without scattering. This result is testimony to the quasi one-dimensional nature of these filaments (carrier scattering is suppressed in one-dimensional systems) and to the possibility of producing reasonably perfect tubes (without too many wall defects). The high mobility of electrons and holes in CNTs were envisioned as a property to be exploited in the fabrication of high-speed semiconducting devices, possibly providing an extension of Moore's law for the time evolution of circuit density in VLSI circuits. Larger diameter multi-walled CNTs have also been recently proposed as interconnects in VLSI circuits. Progress in the development of applications for CNTs in electronics has been encouraging.

CNTs can be produced by many methods. They all require the presence of hot transition metal based nanoparticles (e.g., Fe,Co,Ni and/or their alloys) that act as "seeds" for growth. These particles (sometimes referred to as "catalysts") are placed in contact with a gaseous carbon or hydrocarbon source that deposits carbon on the particle surface. The deposited C atoms then rapidly diffuse toward the base of the tube which grow from the catalyst particle surface. Many of the details of the growth process still need to be elucidated. Growth rates of ~1-10s microns/sec. have been reported. Depending on the nanoparticle diameter, one obtains either an individual single-walled CNT, or SWCNT, orfor larger particle diameters, one can obtain either a bundle of tightly packed SWCNTs or an altogether different structure consisting of a concentric set of tightly nested SWCNTs. In this case, the filament is called a multi-walled CNT, or a MWCNT. The spacing between the walls in a MWCNT is close to the basal plane separation in graphite (~0.34 nm). However, the concentric tube walls are not chemically bonded to one another. Rather, they are weakly coupled by the van der Waals force, so it is possible for one tube to slip within another without structural damage. Finally, MWCNTs can be grown most easily, and they can exhibit many cylindrical shells (as many as ~50) with an inner diameter as small as 1-2 nm and lengths in the tens of millimeters. MWCNTs, as we will learn shortly, are the first CNT to really make it to the marketplace. This success stems in part from the fact that they are easier to grow and in part from the fact that they have been in the R&D process for an additional 10-15 years relative to the SWCNT.

It should be kept in mind that almost all the imaginable applications of CNTs attempt to take advantage of (1) their low mass density, small diameter, and high aspect ratio, (2) their high electron/hole mobility, (3) their high thermal conductivity, and (4) their unusual mechanical properties, i.e., high Young's modulus, fracture toughness, and compliance.

FINDINGS

Large-Scale Production of Bulk CNTs

Based on data collected as part of this study, we find that the current capacity for the production of MWCNTs far exceeds that of SWCNTs. MWCNT capacity is estimated at ~300 tons/yr, compared to ~7 tons/yr for SWCNTs. It should also be noted that the capacity for SWCNTs is far less certain than for MWCNTs and is based on more generalizations, e.g., the amount that might be produced if demand were higher, etc. Most of the production capacity for CNTs is derived from chemical vapor deposition (CVD) methods that use a hydrocarbon gas (e.g., methane) as the carbon feedstock; the catalyst bed in CVD can be either static or fluidized, and the catalyst particle size largely determines the product (e.g., SWCNT or MWCNT). However, a few companies provide SWCNTs produced by pulsed laser vaporization, radio frequency (RF) plasma, or electric arc discharge. Sources in North America appear to have focused more on the production of SWCNTs, primarily by CVD, but also by pulsed laser vaporization, RF plasma, and electric arc discharge.

For both types of CNTs, Asian production capacity is two to three times higher than that estimated for North America and Europe combined. Japan is the clear leader in the production of MWCNTs, with three large companies (Showa Denko, Mitsui, and Hodogaya Chemical) backing the start-up of spin-off companies whose MWCNT production is forecast to exceed 100 tons/yr in the near term. Their MWCNT products appear to differ only in the diameter of the CNT; both companies use a process derived from the "Endo" CVD process, which has evolved considerably over 15 years in Japanese universities through government-

and industry-funded research programs. It should also be emphasized that the Japanese approach to large-scale production of MWCNTs is a continuous (not a batch) process, with the final step involving a high-temperature heat treatment in excess of 2000°C. This treatment eliminates most of the catalyst (by vapor transport) and transforms a rather disorganized carbon filament (called a vapor grown fiber) into a well-ordered MWCNT. In North America, there is only one large producer of MWCNTs, Hyperion; it produces approximately 50 tons/year. Hyperion's tubes do not appear to receive a high-temperature heat treatment and are only sold in master batches, i.e., dispersed in monomer or polymer.

Production of Carbon Nanotubes on Substrates

Both SWCNTs and MWCNTs can be grown directly on substrates by the CVD process by first depositing the growth seeds on the substrate. Several electronics applications, e.g., field effect transistor arrays, field emission sources, and routes to distribute current to various layers of circuits in VLSI chips, are possible using the CNTs where they are grown. In a few cases, R&D is underway to explore the production of large quantities of CNTs (bulk production) by CVD growth from substrates. It was shown early-on that patterned CNT growth could be achieved on Si substrates by selectively removing the oxide. Another approach, of course, is by depositing the catalyst particles only where tubes are desired to be grown. If the catalyst particle number density is sufficiently high, a forest of self-supporting CNTs can be produced (Hata et al. 2004). With carefully controlled growth conditions, the CNT lengths can be 2-10 millimeters. Fujitsu (Japan) is perhaps the world's leading producer of substrate-supported CNT products. In late 2005, it reported the first CNT-based heat sink technology for semiconductor chips (uniform growth over a ~10 inch diameter wafer). It is also involved in the patterned growth of CNT for very large-scale integration (VLSI) (the CNT can support 10^9 A/cm^2 without undergoing degradation due to electromigration).

Large-Scale Dispersion of CNTs

To realize superior mechanical properties of CNT composites, it is essential to be able to uniformly disperse CNTs in the host matrix. The first step in the dispersion process is the appropriate functionalization of the outer CNT wall by adding a molecule that has a strong coupling to the intended solvent. CNT functionalization and dispersion has been a topic of considerable university and industrial research activity worldwide over the last ten years. This research has led to significant intellectual property development. To date, only one company, Zyvex, Inc. (North America), primarily focuses on the development and implementation of technology to disperse nanotubes. CNT dispersions are available, however, from a few CNT manufacturers worldwide. Several companies, e.g., Hyperion, will only transport CNTs in solution.

Mechanical Applications of CNTs

Experiments in the late 1990s indicated that CNTs have a Young's modulus of 1 TPa, i.e., five times larger than the best steel and also five times larger than high-quality carbon fibers. TEM images have shown that CNTs also exhibit remarkable compliance, i.e., the ability to withstand large angle bending without breaking. Because of these remarkable mechanical properties (and low mass density), considerable R&D has been invested in the development of CNT composites, primarily (but not exclusively) with CNT-polymer composites. The incorporated CNTs can also provide electromagnetic shielding and electrostatic discharge benefits. Because of the lower cost and wider availability, MWCNT-polymer composites are now evolving into marketable products.. The primary application for MWCNTs is now in mechanically stabilizing carbon electrodes for Li-ion batteries. In this case, the CNT additive at 5-10 wt% provides a remarkable improvement in the number of charge-discharge cycles before mechanical failure occurs. The nanotubes combat material fatigue encountered during the expansion (charging) and contraction (discharging) as the Li is moved into and out of the carbon electrode. This application alone is forecast to require several hundred tons/yr of MWCNTs in the next few years. The WTEC team observed that the primary Japanese producers of MWCNTs are now in the process of doubling their current production capacity.

Unfortunately, to date, the enhancement of the mechanical properties of the CNT composites attributable to the CNT additive is modest, e.g., the measured tensile strength improves 10-20% and Young's modulus might double but still be 200 times less than that of the CNT itself. Nevertheless, sporting goods with low wt% CNT additions are starting to appear in the marketplace in Japan and the United States. It is not yet clear how the performance of the ski, tennis racket, baseball bat, or golf club is altered or enhanced.

It is also clear that significantly longer CNTs, properly functionalized to covalently bond to the medium, will be needed to use their remarkable mechanical properties. This extra length would allow the fabrication of high modulus yarn, leading to woven CNT fabrics. If this extra length could be achieved, one could envision a large market for CNT composites in military and aerospace applications.

A perhaps unexpected application of a CNT polymer for use as a catheter was previewed to the WTEC panel by Professor Endo during the panel's visit to Shinshu University (Nagano, Japan). Here the unexpected property enhancement through CNT addition was in the surface smoothness and reduced friction of the flexible CNT-polymer catheter. During the panel visit, Prof. Endo also demonstrated that the incorporation of small amounts of CNTs into aluminum alloys dramatically enhanced their thermal conductivity. It seems likely that emerging limited markets will be available soon for both of these applications.

Electronic, Optical, and Optoelectronic Applications

CNTs are being investigated for commercial use in a variety of applications in electronic, optic, and optoelectronic devices. We can divide these applications somewhat artificially by the amount of CNTs required per device. Requiring relatively large amounts of CNTs (milligrams to tens of grams) are Field Emission Devices (FED); composites for electromagnetic interference (EMI) shielding and electrostatic discharge (ESD) protection; additives for battery and supercapacitor electrodes (their role here might only be in enhancing the mechanical stability of the electrodes); and fuel cell electrodes and membranes and transparent, flexible, and electrically conductive screens (e.g., "touch" screens).

We have already mentioned that the Li-ion battery electrode application is currently a commercial reality and a success story for CNTs. It is the primary market driving force for the current increase in MWCNT production capacity in Japan. We suspect that CNT-based supercapacitors will soon become available and will drive the capacity even higher. Team members were unable to secure any significant details on this new market entry, however. Samsung (Korea) has made a substantial investment in developing large-area FEDs based on a forgiving process involving the application of a conductive CNT polymer paste on the back electrode and a subsequent lithographic process to produce the pixels. In this approach, bulk CNTs are used and blended with a polymer to form the paste. There seems to be some uncertainty in the literature as to which CNT is better for FEDs, i.e., SWCNTs, double-walled CNTs (DWCNTs) or MWCNTs. Apparently there is some disagreement over the trade-off between emission efficiency at low device bias versus emission lifetime.

There is also a large market need for cheaper and better transparent electrodes to replace deposited thin films of indium tin oxide (ITO). Several, small start-up companies in North America are developing CNT replacement products for ITO. Flexible and transparent touch screens can be produced by depositing well-dispersed SWCNTs on transparent plastic sheets. Together with FED devices, touch screens may be among the first high-volume applications of bulk SWCNTs.

On the other end of the CNT electronics applications spectrum are devices that require micrograms or less of CNTs. Examples include field effect transistors (FETs) and FET arrays, FET-based or interdigitated resistive chemical and biosensors, and finally, circuit interconnects for VLSI chips (vias). In these cases, it is possible (or required) either to grow the CNTs in place on the substrate or deposit them after growth. For sensors to be "selective" to particular analytes, the nanotubes must either be functionalized to link with specific analytes or be covered with a membrane that passes only the selected analytes. Another application for individual CNTs is high-density logic arrays. Nantero is developing these arrays using individual SWCNTs as electro-mechanical nanoscale random access memory (NRAM) switches that can be held at low power in the "off" or "on" state. Surprisingly, these switches can change state in a few nanoseconds; Nantero claims that it has the technology to deliver these logic gates at high density, and that they can be integrated with complementary metal oxide semiconductor (CMOS) technology. CNT electronic devices have also been grouped together to make fast logic gates or high-frequency (~ 50 MHz) oscillators (for example, by IBM).

CHALLENGES THAT LIE AHEAD

Whereas MWCNTs are definitely making a commercial impact as structural additives in batteries and are poised to enter other markets as well, SWCNTs so far have not made it to the marketplace in substantial quantities, if at all. Part of the reason for this is that MWCNTs are really about 15 years ahead in the R&D curve over SWCNTs. It should be noted that MWCNTs really have their origins in vapor-grown carbon

fibers (VGCFs), which were first made in the late 1970s. Over time, with considerable support from the Japanese government, methods were refined to produce VGCFs at smaller and smaller diameters. SWCNTs, on the other hand, are relatively much earlier in their R&D cycle. The growth of nearly perfect micron-long SWCNTs now has been learned, and these CNTs are being used for the development of electronic devices such as FETs and chemical sensors. However, an inexpensive robust process for the bulk production of high-quality SWCNTs with low fractions of amorphous carbon and residual catalyst is still under development worldwide. When this is accomplished and the cost of bulk SWCNTs drops significantly, we expect many applications to come forward that demand the higher specific surface area (cm^2/gram) provided by SWCNTs. These might include EMI shielding, ESD protection, and conductive flexible transparent electrodes (in touch screens and solar cells).

For the ultimate mechanical/structural applications for CNTs, it remains to be learned how to make significantly longer CNTs in bulk, e.g., hundreds of millimeters in length. When this is achieved, one would expect that the rapid development of first aerospace and then less sophisticated lightweight, high-strength components would eventually become available for general consumers. Realizing the contribution from the remarkable mechanical properties of CNTs will require further development of separation, purification, and dispersion into the host medium, and a means to covalently couple the CNTs to the host.

SWCNTs have been shown to have remarkable electronic properties, e.g., high electronic mobility, ballistic transport at cryogenic temperatures, and a high tolerance to electromigration. In the area of single electronic CNT device applications, it seems to the panel that the most important challenge on the horizon is the production of a truly monodisperse set of SWCNTs, i.e., the production of a gram of material with a predominance of only one type (n,m). The ideal way to achieve this goal would be to learn how to design a catalyst particle that would only produce one chirality. This most likely will occur at a small CNT diameter (d <0.5 nm) where the particle diameter can dominate the (n,m) selection process. A less ideal way to achieve this goal would be to develop separation methods that could first separate CNTs according to metallic or semiconducting tubes and then later be refined to separate tubes according to chirality. The latter step — separation according to one (n,m) — seems to be a significant barrier.

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CHAPTER 1

INTRODUCTION

Peter C. Eklund

BACKGROUND AND SCOPE

Nanotechnology — the design and production of structures, devices, and circuitry at the nanometer scale — represents the cutting edge of many scientific fields ranging from biology to computers. Among the most useful nanostructures created so far are carbon nanotubes (CNTs), which possess a broad range of unique physical, mechanical, and electrical properties. CNTs consist of rolled or coiled graphite sheets (called graphene) with the thickness of a single atom. CNTs can take the form of seamless cylinders of graphene called single-walled carbon nanotubes (SWCNTs), or they can appear as multiple concentric SWCNTs or a single sheet of graphite wrapped around itself, called multi-walled carbon nanotubes (MWCNTs).

Current applications of CNTs — ranging from lightweight space frames and computer chips to scaffolds for the regeneration of damaged nerves — only hint at their broader commercial and scientific potential once they can be manufactured in greater quantities and at significantly lower costs. However, researchers and manufacturers face several challenges in attempting to translate CNT production from the laboratory setting into a commercially viable industry.

The outstanding electrical conductivity of SWCNTs, for example, promises to enable the miniaturization of electronics below the microelectromechanical (MEMS) threshold. SWCNTs can also be used as structural material in both nano- and macroscale applications. However, SWCNTs are much more expensive and difficult to manufacture than MWCNTs, which lack the electrical conductivity of SWCNTs. Unless ways are found to manufacture SWCNTs in commercial quantities and at uniform quality, the promise of CNTs will remain largely unfulfilled.

Many governments, universities, and corporations have launched R&D programs to help bring commercial CNT production to fruition. The United States was among the first countries to recognize the significant potential of CNTs and other nanotechnologies when it launched the National Nanotechnology Initiative (NNI) in 2000. The NNI is a Federal R&D program that coordinates the efforts of 25 Federal agencies in nanoscale science, engineering, and technology. With combined agency budgets of over $1 billion, the NNI has been influential in encouraging organizations in the public, private, and government sectors to invest time and money in CNT R&D. Other countries have since launched similar and even greater efforts. For example, Japan, the country where CNTs were first discovered, recently launched major CNT research programs as part of a broad national nanotechnology R&D strategy. The European Union, through its 2020 Vision program, has done likewise.

Several broad challenges must be overcome to achieve commercially feasible production of SWCNTs:

- Despite recent progress, many properties of CNTs remain poorly understood — particularly the relationship between nanotube species and their resulting electronic, optical, and mechanical properties.
- Basic CNT metrology and commercialization are hindered by the lack of manufacturing methods capable of reliably fabricating CNTs of the same structure and chirality (inability to be superimposed on a mirror image).

- Current fabrication technologies typically result in tangled webs of CNTs, whereas many predicted applications require ordered arrays or streams of CNTs that could be woven into cables or assembled into semiconductors.

To help government decisionmakers and the research community begin to address these challenges, in March 2006 the National Science Foundation (NSF), the Office of Naval Research (ONR), the National Institute of Standards and Technology (NIST), and the National Institute of Biomedical Imaging and Bioengineering (NIBIB) of the National Institutes of Health (NIH) convened the *WTEC Panel on International Assessment of Research and Development of Carbon Nanotube Manufacturing and Applications* to gather and disseminate information on the worldwide status of and trends in CNT R&D. The study was to focus on the manufacture and emerging applications of CNTs as identified by leading researchers around the world.

The objective of the WTEC study was to identify recent progress in understanding the properties and potential of CNTs at academic, industrial, and government research facilities outside the United States. The assessment's sponsoring agencies were particularly interested in manufacturing methods and technologies, technical barriers, test and verification methods, simulation technologies, health hazard identification and mitigation, and opportunities for international collaboration.

This study is timely. Large-scale R&D programs tend to foster both competition and cooperation; the results of this international assessment should help the United States use both means to achieve new successes in CNT R&D.

METHODOLOGY

Once the agency sponsors established the scope of the assessment, WTEC recruited a panel of U.S. experts chaired by Peter C. Eklund, Professor of Physics and Materials Science and Engineering at Pennsylvania State University (see Table 1.1). The assessment was initiated by a kickoff meeting on March 31, 2006, at the NSF headquarters in Arlington, Virginia. Participants discussed the geographic scope and timeline for the assessment, as well as logistical arrangements and the structure and authorship of the final report.

Table 1.1 Panel Members

Panelist	Affiliation
Peter Eklund (Panel Chair)	Pennsylvania State University
Pulickel Ajayan	Rensselaer Polytechnic Institute
Robert Blackmon	Harper International Corporation
A. John Hart	Massachusetts Institute of Technology
Jing Kong	Massachusetts Institute of Technology
Bhabendra Pradhan	Columbian Chemicals Company
Apparao Rao	Clemson University
Andrew Rinzler	University of Florida

The panelists, sponsors, and WTEC convened at the North American Baseline Workshop on June 2, 2006, at NSF to report on electronics applications, production and processing, and government and university R&D in the United States and Canada. Table 1.2 lists the speakers and the titles of their presentations. Full presentations can be found on the WTEC CNM website at www.wtec.org/cnm/.

Table 1.2. Speakers and Presentations at the North American Baseline Workshop

Name	Affiliation	Presentation Title
Peter C. Eklund	Pennsylvania State University	WTEC Study Objectives
Jia Chen	IBM	Carbon Nanotubes for Potential Electronic and Opto-Electronic Applications
Rob Smith	Nantero	Carbon Nanotube-Based Fabrication and Applications Using CMOS Production Techniques
Ji-ung Lee	GE Research	Carbon Nanotube p-n Junction Diodes
Otto Zhou	Xintex	Nanotube X-ray for Biomedical Imaging and Homeland Security Applications
Ken Smith	CNI	SWNT Manufacturing and Emerging Applications
Robert Hoch	Hyperion Catalyst	CNT Production Technology and Research: A Manufacturer's Viewpoint
Benoit Simard	NRC (Canada)	Issues, Barriers, and Solutions for Making High Performance SWNT-based Materials
Nick Andrews	Carbolex	Get on the Curve
Daniel E. Resasco	SW Technologies	Large Scale Production of SWNT at SouthWest Nanotechnologies
Mark Banash	Zyvex	Carbon Nanotube Applications
Enrique Barrera	Rice University	Functional Carbon Nanotube Composite Materials
Daniel Geohegan	Oak Ridge National Laboratory	Overview of Carbon Nanotube Synthesis, Research, and Development at Oak Ridge National Laboratory
Robert Hurt	Brown University	Toxicology of Carbon Nanotubes

The international assessment phase commenced with a one-day workshop in Tokyo at the International Center on September 25, 2006 (speakers are shown in Table 1.3), followed by a week of visits to the 19 sites shown in Table 1.5. Site visit hosts demonstrated a wide range of CNT-related R&D activities. Several institutions appear to be actively gearing up for commercial production of CNTs, while others that are currently predominantly research-oriented appear to be considering scaling-up to production as well. Other facilities actively use CNTs in a variety of products ranging from computer chips to consumer goods. The site visits concluded with a one-day U.S.-China Workshop on Carbon Nanotube Manufacturing R&D held at the Friendship Hotel, Beijing, China, on September 28, 2006 (Table 1.4).

Table 1.3 Speakers and Presentations at the Japan Workshop

Name	Affiliation	Presentation Title
Yuji Ozeki	TORAY Industries, Inc.	Research and Development of SWNT and DWNT in Toray
Koji Ishibashi	RIKEN	Artificial Atom in Carbon Nanotubes And its THz Response
M. Endo	Shinshu University	Large Scale Production and Applications of Carbon Nanotubes in Japan
Masahiro Takemura	National Institute for Materials Science	National Nanotechnology Projects of Japan
Junji Haruyama	Aoyama Gakuin University	Superconductivity with T_c = 12K in Entirely End-bonded Multi-Walled Carbon Nanotubes
Fumio Kokai	Mie University	Laser-based Carbon Nanotube Studies
Susumu Saito	Tokyo Institute of Technology	Predictive Quantum Theory for Carbon Nanotubes: Its Importance in Nanoscience and Nanotechnology

Table 1.4 Speakers and Presentations at the China Workshop

Name	Affiliation	Presentation Title
Fei Wei	Tsinghua University	Mass Production of SWCNTs
Zuolong Yu	CAS Chengdu Institute of Organic Chemistry	Application of Carbon Nanotubes in Batteries
Huiming Cheng	CAS Institute of Metals	Nanotube Synthesis and Applications
Yongsheng Chen	Nankai University	Optical Applications
Yunqi Liu	CAS Institute of Chemistry	Preparation and Electronic Devices of MWCNTS
Kevin Lyons	NSF	An Overview of NSF Efforts to Support Research in Nanotechnology and Carbon Nanotubes
Zheng Hu	Nanjing University	About The Growth Mechanism of CNTs
Yan Li	Peking University	Synthesis of SWCNTS on Surfaces
Jin Zhang	Peking University	Ultra-Long Single-Walled Carbon Nanotubes
Xiaogang Sun	Sun Nanotech Co., Ltd.	Commercialization of CNTs
Xin Li	Xi'an Jiaotong University	FEDs
Lianfeng Sun	National Center for Nanoscience and Technology	Synthesis and Characterization of Single-walled Carbon Nanotube Rings
Zujin Shi	Peking University	Filling CNTs
Khershed Cooper	Office of Naval Research	A View of Nanotechnology and Carbon Nanotube Research from the Perspective of National Labs

Table 1.5 Sites Visited in Asia

Host Name	Site	Host Name	Site
Dr. Morio Yumura Dr. K. Hata	Advanced Industrial Science and Technology (AIST)	Dr. Young Chul Choi You Jong Kim Ilhwan Kim	Samsung SDI Co., Ltd.
Dr. Sishen Xie Dr. Li Lu Dr. Lianfeng Sun Dr. Li Song	Institute of Physics, Chinese Academy of Sciences (IOP-CAS)	Prof. Young June Park Prof. Yong Hyup Kim Prof. Yungwoo Park Prof. Seonghoon Lee	Seoul National University (SNU), NANO Systems Institute (NSI)
Prof. K. Kaneko	Kaneko Research Lab	Chuanyi Zhang	Shenzen Nano-Technologies Port Co., Ltd. (NTP)
Taek-jung Shin Sungwoo Byun Shin-je Cho	Iljin Nanotech	Prof. Morinobu Endo	Shinshu University
Hiroshi Sato Shoji Kawashima Fuminori Munekane	Nano Carbon Technologies Co., Ltd. (NCT)	Dr. Yoshiyuki Nishimura	Showa Denko (SDK)
Dr. Zhong Zhang Zhihua Ji	National Center for Nanoscience and Technology (NCNST)	Mr. Xiaogang Sun Mr. Xiaoshu Zeng	Sun Nanotech Co., Ltd.
Dr. Masako Yudasaka	NEC Corporation (NEC)	Prof. Shoushan Fan Dr. Changhong Liu Dr. Qunqing Li Dr. Kaili Jiang Dr. Liang Liu	Tsinghua University, Tsinghua-Foxconn Nanotechnology Research Center (TFNRC)
Dr. Zujin Shi Dr. Jin Zhang Xiaojie Duan Wang Jingyun Dr. Yan Li	Peking University, Center for Nanoscale Science and Technology (CNST)	Dr. Wei Fei Dr. Qian Weizhong	Tsinghua University, Beijing Key Lab of Green Chemical Reaction Engineering and Technology
Dr. Koji Ishibashi Dr. Kohei Tamao	RIKEN (The Institute of Physical and Chemical Research)	Dr. Kyung-Hwa Yoo Prof. Jungho Hwang	Yonsei University Yonsei Nanomedical, National Core Research Center

Following the site visits, the panel reconvened for a final workshop at NSF on November 3, 2006, to present its findings and conclusions. Presentations focused on methods for scaling-up CNT production, separation, and purification; dispersion, functionalization, blends, ordered arrays, and single replacement; mechanical and electronic applications; and broader issues identified by the panel during the assessment.

OVERVIEW OF THE REPORT

This report broadly follows the outline of the November 2006 workshop. In Chapter 2, Robert Blackmon and Andrew Rinzler review recent attempts to produce CNTs at a commercial scale in Asia and North America, noting that many firms are implementing sophisticated processing techniques to add value to their CNT

products. Chapter 3 presents Bhabendra Pradhan's analysis of post processing of CNTs for a variety of research and consumer applications, and it identifies areas where additional research is needed. Apparao Rao examines the promising technologies for the synthesis of MWCNTs and SWCNTs and also discusses emerging applications in Chapter 4. In Chapter 5, Pulickel Ajayan reviews the mechanical properties of CNTs that make them suitable for applications ranging from advanced polymer, metal, and ceramic matrix composites to MEMS technologies and mechanical stabilizers. Finally, A. John Hart, Andrew Rinzler, and Jing Kong discuss in Chapter 6 the practical applications for CNTs in electronics and optoelectronics, depending on their diameter and chirality, and taking advantage of their inherent mechanical and thermal stability.

Appendix A contains vitas of the panelists, and Appendix B includes detailed reports for each of the sites visited during the international assessment.

Additional information and documentation and photographs for all phases of the *WTEC International Assessment of Research and Development of Carbon Nanotube Manufacturing and Applications* are available on the WTEC website at www.wtec.org/cnm/.

CHAPTER 2

SCALING-UP OF CNT PRODUCTION, SEPARATION, AND PURIFICATION

Robert Blackmon and Andrew Rinzler

BACKGROUND

In recent years, production of carbon nanotubes has begun to migrate from a research-focused laboratory scale to nascent industrial scale production. In many instances, initial attempts at industrial scale production have followed techniques developed at the laboratory scale. In other instances, efforts have been made to use scaled-down versions of industrial production techniques at the laboratory scale. Critical operating parameters, such as selection of catalyst material, carbon sources, materials of construction for production equipment, type of production equipment, and mode of operation (semi-batch or continuous) are being explored and defined at the industrial scale. The following discussion gives a basic overview of the industry as it exists today in both North America and Asia. Key challenges for continued growth and reduced production cost and the steps that have been taken to meet those challenges are identified.

THE STATE-OF-THE-ART IN CNT PRODUCTION: CAPACITY

To begin a discussion of the state-of-the-art in CNT production, it is useful to first provide an overview of the bulk production capacity that is available worldwide. The North America workshop conducted by WTEC in June of 2006 and site visits to worldwide facilities in September of 2006 have been used to estimate the total worldwide bulk production capacity of CNTs. The estimated production capacity for MWCNTs is presented in Table 2.1; the summary for SWCNTs is presented Table 2.2.

Table 2.1. Estimated Worldwide MWCNT Production Capacity, 2006

Geography	Country	Company	Capacity (kg/hr)	Capacity (tpy) *	Note Regarding Capacity
Asia	China	NTP	5	10	Reported as 40 kg/day -- 10 tpy
Asia	China	Sun	0.625	5	Reported as 5 kg/8 hours -- 5 tpy
Asia	China	Tsinghua (Prof. Fei Wei)	15	15	Reported as 15 kg/hr -- 15 tpy (Annually 1500 hrs operating)
Asia	Korea	Iljin	10	10	Reported as 10 kg/month -- 1 kg/hr max instant
Asia	Japan	NCT	5	30	Reported as "Some kg/hr" -- Year 2007 to be 100 tpy
Asia	Japan	Showa Denko	16.7	100	Reported as 40 tpy in yr 2000 -- Expansion to 100 tpy in 2006
Europe		Not Disclosed	0.833	5	Estimated Range
Europe		Not Disclosed	2.5	15	Estimated Range
Europe		Not Disclosed	0.167	1	Estimated Range
Europe		Not Disclosed	1	6	Estimated Range
North America	USA	Hyperion	8.3	50	Capacity Estimated at more than 50 tpy.. Hyperion did not disclose capacity to WTEC
North America	USA	Not Disclosed	4	24	Estimated Range
North America			12.3	74	
Europe			4.5	27	
Asia			52.3	170	
Total Capacity			69.1	271	

* Unless reported otherwise by the host, the total Annual Capacity estimted based on 6000 operating hours per year.
* The quality of the product at estimated Annual Production may not be optimal.
* Annual Capacity estimate is speculative if the systems are not operated in continuous mode.

Table 2.2 Estimated Worldwide SWCNT Production Capacity, 2006

Geography	Country	Company	Capacity (g/hr)	Capacity (kg / yr) *	Note Regarding Capacity
Asia	China	NTP	85	*500*	Estimated at 500 kg per year
Asia	China	Tsinghua (FW)	1000	*1500*	Reported as 1 kg/hr. Annual Capacity based on 1500 op. hours
Asia	Korea	Iljin	1.25	2.4	Reported as 200 g/month
Asia	Japan	Toray	15	1500	Reported as "100s kilos per year within coming years"
Asia	Japan	Mitsubishi	200	1200	Reported as 200 g/hr
Asia	Japan	Hata	100	600	Estimated at 100 g/hr
Europe		Not Disclosed	---	100	Range Unknown -- Estimated at 100 kg / year
North America	USA	CNI	65	113	Reported as 1 lb/day
North America	USA	SWeNT	6	12	Reported as 1kg / month
North America	USA	Carbolex	100	600	Reported as 100 g / hr
North America	Canada	NRC-CNRC	120	720	Reported as 2 g / min
North America	USA	Nano-C	2	12	Reported as 4 - 30 g / day
North America			**293.0**	**1457**	
Europe			**0.0**	**100**	
Asia			**1401**	**5302**	
Total Capacity			**1694.3**	**6859**	

 * Unless reported otherwise by the host, the total Annual Capacity estimted based on 6000 operating hours per year.
 * The quality of the product at estimated Annual Production may not be optimal.
 * Annual Capacity estimate is speculative few systems are operated in continuous mode.

The capacity for MWCNT production worldwide in 2006 is estimated at approximately 270 tons/year. The production capacity for SWCNT worldwide in 2006 is estimated at less than seven tons/year. The estimates for SWCNT production are made using broad generalizations about the theoretical production rate if facilities were to operate in continuous fashion. In most cases, the production of SWCNT is managed on an as-needed basis; no facilities are running continuous production of SWCNTs due to lack of demand for the product at the still comparatively high prices.

The production capacity of both MWCNTs and SWCNTs currently appears to be dominated by Asian, primarily Japanese, manufacturers. Dominance in the field of SWCNT production appears to have shifted toward Japan. Overall, the production rates of MWCNTs appear to be in line with previous projections. The production rates of SWCNTs do not appear to meet previous projections. Growth in SWCNTs has primarily come through Japan's research and production efforts.

THE STATE-OF-THE-ART IN CNT PRODUCTION: TECHNIQUES

The levels of sophistication of the production techniques used by manufacturers of CNTs vary greatly within geographies. The production techniques used by various companies within Asia are presented below.

Asia

The production methods used by companies within Asia vary, but in general, the dominant technique is CVD growth in a quartz tube furnace. This equipment style is common throughout academia and within the companies dedicated to bulk production of CNTs. Less consistent among the producers in Asia are the production goals and the postproduction purification steps employed by the various companies.

China

Three principal producers of bulk CNT materials were identified prior to the WTEC trip to Asia. The major producers within China appear to be Sun Nanotech Co, Ltd., Shenzhen NanoTechnologies Port Co., Ltd. (NTP), and Professor Fei Wei's group at the Department of Chemical and Reaction Engineering at Tsinghua University. The study tour included discussions with each of these groups.

Although capable of production rates nearing 15 tons/yr, the facility at Tsinghua University is not currently organized towards commercial production. Instead, this facility frequently produces batch runs of CNTs as part of collaborative ventures. Sun Nanotech uses tube furnaces to produce its materials (Figure 2.1). NTP uses a continuous cycle pusher, or belt-type furnace, to produce its materials (Figure 2.2).

Figure 2.1. Production system at Sun Nanotech.

Figure 2.2 Production system at NTP.

Both Sun's and NTP's systems appear to rely on a high degree of manual operator intervention for production (i.e., manual extraction of tubes after a production run). The cyclical pusher type furnace system at NTP can be seen as an automation advance over the growth of MWCNT or SWNT on a bed of catalyst in a static quartz tube furnace.

These systems appear to be a straightforward evolution of lab-scale predecessors such as the units shown in Figures 2.3 and 2.4 from research laboratories at Peking University and Tsinghua-Foxconn Research Center.

Figure 2.3. CVD-based quartz tube CNT units at research laboratories at Peking University.

Figure 2.4. CVD-based quartz tube CNT units at research laboratories at Tsinghua-Foxconn Nanotechnology Research Center, China.

Professor Fei Wei's group at the Department of Chemical and Reaction Engineering at Tsinghua University has focused research and efforts on the production of CNTs using fluid bed technology. The fluid bed device housed at that facility is a 500 mm diameter, metallic (stainless steel) process system. Professor Fei Wei's group has focused significant efforts on the development of continuous processing techniques that lend themselves well to industrial scale-up. The process reactor shown in Figure 2.5, housed at the facility at Tsinghua University, includes gas-solid separation techniques, reactor load/unload techniques, and even product densification techniques. The group claims to have developed a method for five-fold volume reduction of the product, allowing for expansion and dispersion at a later time with little to no loss in product quality. In general, the group's work in MWCNT production follows a comprehensive approach that includes ancillary steps often ignored by institutes focusing on materials property research. In addition to investigation of these auxiliary process units, its work demonstrates the production of CNTs in a process unit constructed of stainless steel rather than the typical quartz or ceramic construction. It should be pointed out that although this work appears to entail significant advances in scaled-up production, there is no independent information presented here regarding the quality of the nanotubes produced from any of the manufacturers.

Due to the variety of industrial partners involved in research at Tsinghua University, Professor Fei Wei's group claims that a large part of the development cost associated with CNT work at his facility is development of client-specific catalysts or techniques, providing each partner with a processing route that is unconstrained by intellectual property rights. Professor Fei Wei indicated that his group has worked with over 20 different types of catalysts, all typically variations of metal support on a carrier. Ms. Christine C.Y. Zhang, representative of NTP, also made the point that a major cost of production was in the research and development of tailoring the product to the customer's needs.

Figure 2.5. CVD-based fluid bed unit in stainless steel materials at Tsinghua University.

Korea

A prominent group within Korea working on the bulk production of MWCNT materials is Iljin Nanotech, a start-up venture funded by the Iljin Group. Iljin Nanotech has focused on the production of CNT material using a variety of techniques including arc and CVD growth (static and fluidized bed-based CVD). Their work includes patents for belt CVD, arc, vacuum CVD, and rotary plasma type furnaces. The primary technique of interest to Iljin at this time is CVD growth in quartz tube furnaces.

Iljin has dedicated a significant amount of research toward the optimization of the CVD reaction, with a push toward MWCNTs possessing few walls (growth of double-wall or triple-wall CNT mixtures). Arc production has been used by Iljin to develop SWCNTs. Iljin has begun work in fluid bed reactors for production of MWCNT products.

Iljin considers itself well-positioned in terms of intellectual property (IP) with a wide variety of patent applications and issued patents in Korea, United States, Europe, China, and Japan (Table 2.3).

Table 2.3. Patent filings by Iljin Nanotech

Patents	Korea	U.S.	Japan	EU	China
Applied	49	15	15	15	15
Granted	36	2	1	---	---

The WTEC panel was not allowed access to the production facility for Iljin. Therefore, photos of the production systems used by Iljin, are not available. Iljin focuses a significant portion of its research toward the growth techniques and postproduction techniques. The company has research efforts in the area of application of CNT materials to Field Emission Devices, including marketing of materials to other groups within Korea that focus on FED work. Iljin also has an internal effort focused on the development of CNT-based FEDs.

Japan

Within Japan, two groups have focused on mass production of MWCNT materials. Nano Carbon Technologies (NCT) — a joint venture between Hodogaya Chemical Co., Ltd., and Mitsui Co., Ltd. — and Showa Denko both produce MWCNT materials and post-process MWCNT materials for specific applications: composites and battery additives. The work of both groups stems from research pioneered by Prof. Morinubo Endo of Shinshu University.

Knowledge of the production equipment is limited to the understanding that both groups utilize a floating-catalyst CVD technique (operating at approximately 700°C). In addition, both groups have specialized in sophisticated postproduction techniques for improvement of the as-produced material. The post processing involves a single or double stage of high-temperature (up to 2600°C) thermal annealing of the material after growth in a CVD furnace. The thermal annealing process and the CVD furnace are reportedly incorporated as a single operating unit as opposed to being distinct processing steps.

The post processing techniques, although undoubtedly adding significant production cost to the material, appear to generate substantial improvement in the MWCNT wall crystallinity over the as-produced state. Figure 2.6 gives an indication of the improvement in the tube wall structure. Unlike their contemporaries in Asia, these two groups in Japan appear to have focused on high-quality, thick-walled MWCNTs rather than thin-walled MWCNTs.
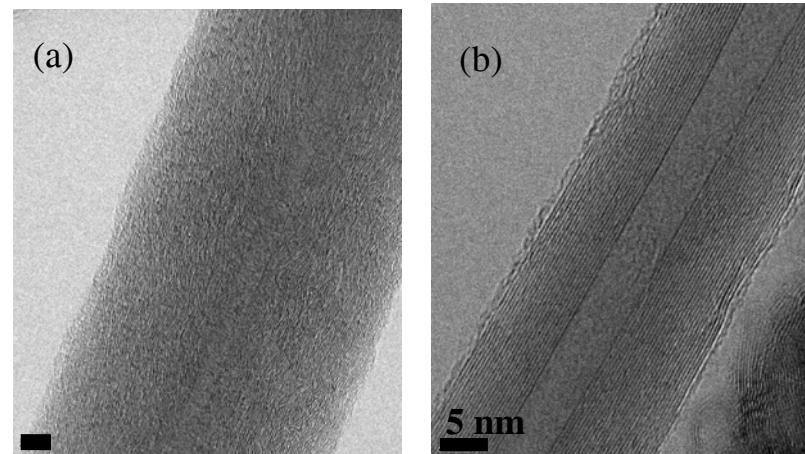
Figure 2.6. High-resolution transmission electron microscopy (HRTEM) images of (a) bulk-grade MWCNT; (b) high-purity-grade MWCNT (Courtesy of Dr. Kim at Shinshu University).

Within Japan, another facility, Toray industries, has also begun work on MWCNT production. Much of Toray's efforts are directed toward application development. Reportedly, Toray utilizes a CVD technique for CNT production. Much of its research is focused on the development of DWCNTs and applications using its products (thin films, polymer blends, specialty fibers).

North America and Europe

North American and European producers of bulk CNT materials seemed to have focused on production techniques distinct from the trends set by Asian counterparts. Whereas in Asia the use of the horizontal quartz tube furnaces is prevalent in research and production facilities, in North America and Europe, the quartz tube furnace (rotary or stationary) is relatively uncommon outside of the academic arena. Producers of CNTs within North America and Europe have focused on techniques more closely related to rapid transport and fluid bed type reactor systems for CVD-based production or have focused on non-CVD techniques, such as the arc process. Further, with the exception of one or two well-known suppliers of MWCNTs, facilities in North America appear to be more focused in research and production of SWCNTs rather than MWCNTs. Several of these facilities are highlighted in Figures 2.7-2.9.

2.7. Pilot plant production system at SouthWest Nanotechnologies (SWeNT) (Resasco 2006).

Figure 2.8. High-pressure CO conversion (HiPCO) process,
Carbon Nanotechnologies, Inc. (CNI) (Smith 2006).

Figure 2.9. RF Plasma process, University of Sherbrooke (Simard 2006).

GAPS BETWEEN EXISTING KNOWLEDGE AND REQUIRED CAPABILITIES

Commercialization efforts made to date appear to be guided largely by IP restrictions and process knowledge gained at the laboratory scale. A nearly unanimous opinion held within the field is that the scant availability of applications that use CNTs has limited the growth of CNT production. In general, for MWCNTs, industry experts believe that the bulk production techniques necessary to support mass CNT production are available and that growth in production systems will follow a demand for the product.

Potential gaps appear to exist, however, in the knowledge base regarding CNT bulk production. The potential of these gaps could influence the future of CNT manufacturing and, subsequently, the cost of CNT-enabled products. For example, numerous production systems are built around the concept of using non-metallic materials of construction for the process reactor, i.e., quartz or ceramic materials. However, some producers and researchers use metallic (stainless steel) construction for their production systems. Non-metallic materials of construction add to the cost of the manufacturing equipment and consequently to the cost of the final product. This cost burden will become greater as production rates continue to scale up because of limitations to the physical size and configurations available for ceramic or quartz materials of construction. Fundamentally, the question of materials of construction for future production systems has not been concretely evaluated or answered.

This gap in the knowledge base and other discontinuities in current production techniques and industry practices are itemized below:

1. There needs to be a comprehensive evaluation of the influence of metallic materials of construction on the quality of CNT products. Can metallic materials be used in lieu of more complex and costly non-metallic materials to construct CNT production systems? Do metallic systems unacceptably contaminate the product? Will metallic materials unacceptably deteriorate or corrode during production, resulting in limited equipment lifetimes?

2. Can a set of internationally accepted standards be developed and adopted to quantify the quality of CNT products? Individual countries have begun efforts at standardization. Can an international effort be organized? Does an international effort have merit?

3. At the production scales explored to date, the cost of catalyst for CVD production can represent as much as 20%–50% of the cost of the product. Methods for reducing the cost of catalyst will need to be developed to achieve long-term reduction of CNT production costs. Do IP restrictions and patent applications limit the possibility of reducing the catalyst cost?

4. The common long-term vision is that CNTs will be a bulk material market on the order of thousands of tons/year. Where CNTs are directly added into master batches, the material handling and shipment of the CNTs is straightforward. For applications that require dry dispersed CNTs, the potential volume CNT product presents a transportation and logistical conundrum. To date, few organizations have investigated and developed a means to realize volumetric reductions prior to product shipment. What techniques are needed to allow shipment of thousands of tons of CNTs around the world?

The issues above represent areas where additional study and investment will help to lower the costs associated with CNT products.

Despite the commonly held belief that the price of CNT production needs to come down significantly for applications to emerge and production demand to grow, it is interesting to note that two of the largest producers worldwide (Showa Denko and NCT) both use a costly, high-temperature thermal annealing step for their products. Although the expense added to the production cannot be doubted, the companies have seen application-related success and notable improvement in product quality by using this additional processing step.

Figure 2.10 gives a summary of the IP and patent filings related to CNT at the time of this WTEC study. Interestingly, the largest applications at this time, composites and batteries, equaled only 20% of the overall IP efforts. At the time of publishing, the largest IP activity was related to CNT synthesis and processing techniques.
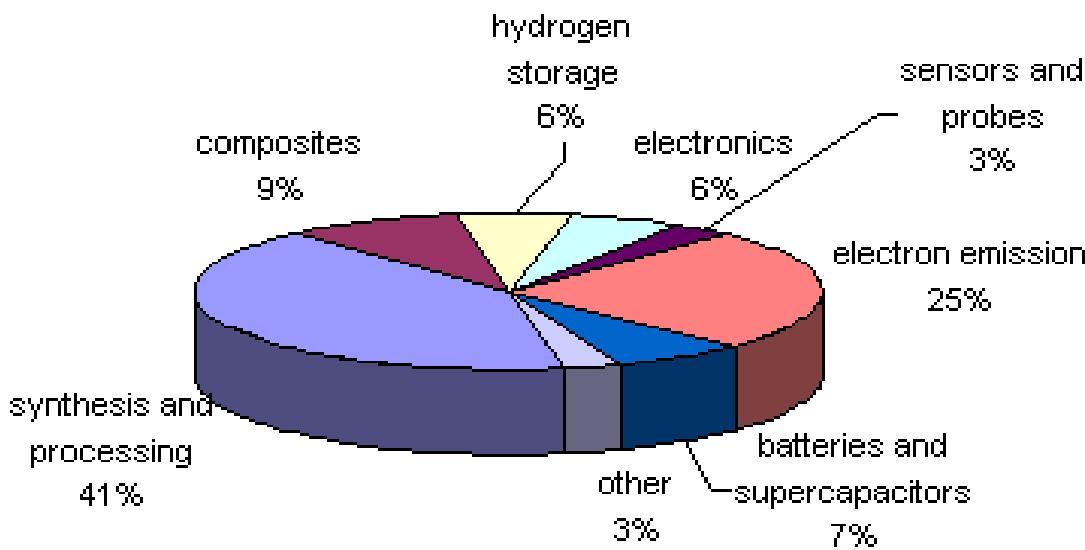
Figure 2.10. International patent of CNT filings and issuances (*Science* 2002).

From discussions held with our hosts during the WTEC study, it appears that little concern is placed on the status of IP restrictions in relation to the production techniques. At the institute level, most researchers view the synthesis reaction and the components of the reaction (carbon source, catalyst, and equipment type) with little interest. There does not seem to be motivation or desire to investigate new or novel production routes that may be free of IP restrictions or may offer distinct avenues to production.

Researchers who are concerned with IP restrictions seem to view the task of finding a distinct catalyst or distinct set of processing parameters to avoid IP as a necessary evil and a burden. Other than adding time to the cycle of innovation and research, IP restriction does not seem to offer distinct advantage. Many researchers and companies have adopted tight nondisclosure policies to protect their trade secrets rather than rely on patent filings and IP positioning.

SUMMARY AND CONCLUSIONS

Tables 2.4 through 2.7 provide the WTEC panel estimate of worldwide status of industrial production. A common theme encountered during the WTEC study is that applications (or the lack of applications to spark demand) are the only obstacles to the pending expansion in production of CNTs. Future scale-up will require additional research and development into processing techniques if cost reduction is desired at larger production scales. Although many of the processes employed are built on the backbone of conventional equipment, there are vital lessons to be learned with regard to the real IP restrictions that may come into play, materials of construction, materials handling, and health and safety. These lessons are likely to be learned at the expense of the industrial partners who push production capacity forward. Research at the institute level could ease this growth period and aid in industrialization. This needed research will likely be seen as a secondary priority to the single largest challenge: development of applications to create uses and demand for CNT materials.

The WTEC study has served to provide an overview of the processes used by the various production companies present in the marketplace at this time. The study has also given an indication of the trends in production, shedding light on the number of producers that are pursuing thin walled carbon nanotubes versus pursuing sophisticated post-processing techniques to add value to their products. It would be useful for researcher, manufacturers, and product users to have a standard reference for products. A concerted effort must be made to have a common analytical sampling of the various bulk products that are available in the market. Analysis of the various products at a common lab facility using identical lab procedures will help to identify quality differences in the various products that are available. These quality differences may reveal combinations of techniques that lead to higher-quality and lower-cost bulk CNT production.

Table 2.4. Asia and Europe: Summary of the Current Production Capacity and Techniques Available

Company	Geography	Country	Capacity MWCNT (tpy)	Capacity SWCNT (kg/yr)	Note Regarding Capacity	Technique	Catalyst	Specialty	Post Processing	Other Experiences
NTP	Asia	China	10	500	As Reported	CVD Pusher	Supported Metals	SW, DW, TW and MW CNTs		Control of Dia. and Wall through Feedstock and Process
Sun	Asia	China	5		As Reported	CVD Tube	Supported Metals	MWCNT	Washing in Salt Acid	
Tsinghua (FW)	Asia	China	15	1500	As Reported	FB CVD	Supported Metals (Various)	MWCNT	Thermal Annealing	Packaging Techniques, Composites, Metallic Construction FB
Iljin	Asia	Korea	10	2.4	As Reported	CVD /Arc	Supported Metal	Thin Walled (Double and Triple Wall)	Acid Washing	In House FED Applications
NCT	Asia	Japan	30		Estimated Range (2007)	CVD - Endo Process (FB)	Presumed Floating	High Purity MWCNT	High Temperature Annealing	Master batches, Batteries
Toray	Asia	Japan		1500	Estimated Range -- Reported as "100s kilos per year within the coming years"	CVD	Supported Metals - Zeolite	Double Wall	Dispersion Techniques	Films, Specialty Fibers, Polymers
Mitsubishi	Asia	Japan		1200	Reported As 200 gr/hr					
Hata	Asia	Japan		600	Estimated at 100 gr/hr					
Showa Denko	Asia	Japan	100		As Reported	CVD - Endo Process (FB)	Floating	High Purity MWCNT / nCF	High Temperature Annealing	Master batches
Multiple Producers	Europe		27	100	Estimated at 100 kg/yr	Assumed CVD, Others	Assumed Supported Metals			

Table 2.5. North America: Summary of the Current Production Capacity and Techniques Available

Company	Geography	Country	Capacity MWCNT (tpy)	Capacity SWCNT (kg/yr)	Note Regarding Capacity	Technique	Catalyst	Specialty	Post Processing	Other Experiences
Hyperion	North America	U.S.	50		Estimated Range	FB CVD	Supported Metals	Fibrils (As Produced MWCNT)		Master batches, Dispersion Techniques
Not Disclosed (Multiple Producers)	North America	U.S.	24		Estimated Range	Assumed CVD, Others	Assumed Supported Metals			
CNI	North America	U.S.		113	Reported as 1 lb / day	HiPCO	Floating	SWCNT		
SWeNT	North America	U.S.		12	Reported as 1 kg/month	CVD	MoCat (Mo Co Silica)			
Carbolex	North America	U.S.		600	Reported as 100 gr/hr	Arc	Metals in Graphite Electrode	SWCNT	Washing / Dispersion / HVTA	
NRC-CNRC	North America	Canada		720	Reported as 2 gr/min	RF Plasma and Laser	Metals	SW, DWE, MW CNT		
Nano-C	North America	U.S.		12	Reported as 4 - 30 g/day	Flame Spray	Floating	SW, Fullerenes	Acid Treatment and Air Oxidation	

Table 2.6 Geographic Totals

Geography	Capacity MWCNT (tons/year)	Capacity SWCNT (kg/yr)
North America	74	1457
Europe	27	100
Asia	170	5302.4
Total Capacity	271	6859

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CHAPTER 3

DISPERSION, FUNCTIONALIZATION, AND CNT BLENDS

Bhabendra Pradhan

The exceptional physical and mechanical properties of CNTs are driving their use in numerous fields, not limited to composites for structural and electronic applications. These applications range from mixing of a few weight-percent of MWCNTs or SWCNTs in a polymer matrix for enhancement of electrical conductivity and structural properties. The success of these applications depends on their ability to be dispersed and on the surface chemistry of CNTs in the matrix in order to achieve the desirable properties. This chapter gives an overview of the promises and challenges of post processing of carbon nanotubes i.e., dispersion, functionalization, and blends for composites, mainly for electrostatic (ESD and EMI) or structural (sporting goods) applications.

BACKGROUND

Carbon nanotubes have particular physical properties that exceed those of commonly used materials. For example, a tensile strength eight times that of stainless steel and a thermal conductivity five times that of copper make CNTs an obvious choice for creating a new class of composite materials for a variety of applications (Dresselhaus, Dresselhaus, and Eklund 1996; Ebbesen 1997). Their inclusion in a polymer such as polyurethane holds the potential to boost the host material's electrical, mechanical, or thermal properties by orders of magnitude above the performance possible with traditional fillers such as carbon black or ultrafine metal powders.

One of the technical hurdles associated with CNTs is post-synthesis, i.e., dispersion of CNTs in the matrix. While a large knowledge base exists for incorporating micron-sized carbon-based fibers or nanosized carbon black in a host, very little has been done to optimize the incorporation of CNTs into the matrix. Certainly in the past few years as CNT supplies have become more abundant, more efforts to successfully process CNTs using extrusion (Sennett et al. 2003), ultrasonic process (Qian et al. 2000), and high shear mixing and melt spinning (Jin et al. 2001) have been developed to overcome this problem. Dispersion of the tubes is particularly important. Failure to disperse produces a phase separation due to the strong surface interactions between the tubes. It is likely that chemical functionalization would not only serve to facilitate dispersion but could also stabilize the CNTs and prevent agglomeration.

Although CNTs have exceptional chemical and physical properties, incorporating them into other materials has been inhibited by the chemical nature of their side-walls. In many applications, it is necessary to tailor the chemical nature of the nanotubes in order to take advantage of their unique properties. In the area of material chemistry, for example, problems such as phase separation, aggregation, poor dispersion within a matrix, and poor adhesion to the host must be solved (Figure 3.1). These problems can be addressed by developing a new multifunctional surface treatment technology that optimizes the interaction between CNTs and the host matrix, according to Dr. M. Banash of Zyvex (2006).
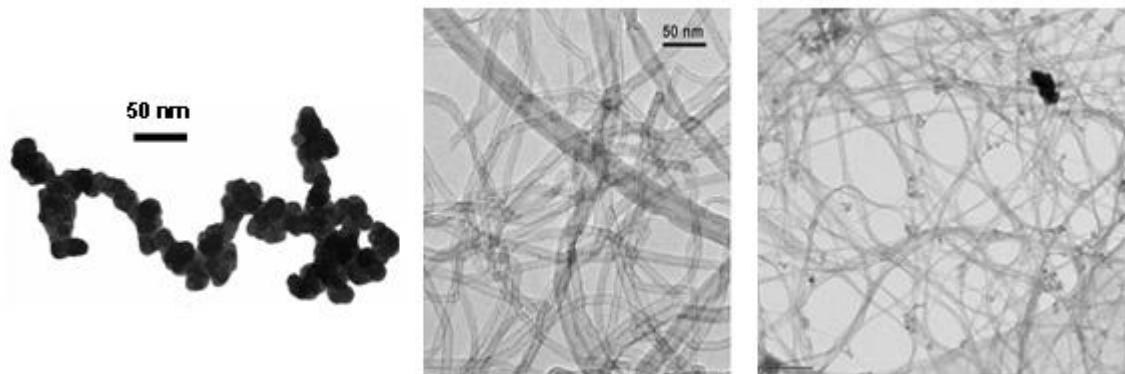
Figure 3.1. Agglomeration of carbon nanomaterials is a problem: carbon black, MWCNTs, and SWCNTs.

Due to strong attractive interactions, and van der Waal interactions, almost all the carbon nanomaterials form an aggregate, and without any exception, SWCNTs tend to aggregate to form ropes or bundles and further agglomerate when dispersed in a polymer matrix, thus preventing the efficient transfer of their superior properties to the matrix. The high surface area of the nanotubes also results in high viscosity of the nanotube/polymer mixture that makes it extremely difficult to form a uniform dispersion. In addition to needing to obtain uniform dispersion of the nanotubes within the polymer matrix, it is critical to obtain a structure of the nanotubes in the resulting composites.

CNTs synthesized by arc discharge, laser ablation, or chemical vapor deposition processes require purification because raw products are usually a mixture of nanotubes, other carbonaceous materials, or metal catalysts, etc. After purification, nanotube fibers have a particular length distribution and side-wall surface chemistry, which depends on the production method and purification conditions. A more significant condition for raw and purified nanotubes is that they are arranged in bundles held together by van der Waals forces on the lines of contact along the tube length. In particular, these intermolecular forces of attraction are based on a π-bond stacking phenomenon between adjacent nanotubes (Chen et al. 2001). Because there can be hundreds of π-stacking sites between two SWCNTs, intermolecular forces are stronger than those found between two relatively small hydrocarbon molecules. However, when nanotubes are made to slide along their length, resistance is lower than what is normally found in entangled polymeric molecules. Thus, nanotubes are normally found in the form of bundles, which have to be processed and/or functionalized into dispersed individual SWCNTs. This is especially true if the nanotubes are going to be used to reinforce polymeric materials. If other properties of nanotubes are desired, such as their excellent electrical and enhanced thermal properties, then a lower level of dispersion might be good enough, even though there were some degradation of the overall mechanical properties.

In order to understand the physical dispersion of SWCNTs, the molecular thermodynamics concepts have to be considered. The Gibbs energy change per mole, ΔG, is a quantity that determines whether a material is soluble in a mixture. ΔG needs to be negative in order to obtain miscibility in a mixture (Prausnitz, Lichtenthaler, and de Azevedo 1999). ΔG is relative to that of the pure components (SWCNT/MWCNT and solvent). Since the Gibbs energy change is an abstract quantity, it is represented as a relation involving the enthalpy and entropy. Thus, $\Delta G = \Delta H - T\Delta S$, where ΔH and ΔS are the enthalpy and entropy change, respectively. Again, both ΔH and ΔS are measured relative to their pure components. In order to obtain miscibility (or dispersibility for carbon nanotubes), ΔH should go down, and/or ΔS should go up. When ΔH decreases, other molecules that preferentially interact with the carbon nanotubes have to be present. When ΔS increases, a preferentially ordered structure between the carbon nanotubes and other molecules in the mixture is required.

Based on this thermodynamics, it should not be a surprise that hydrocarbons are not capable of dispersing carbon nanotubes. They rely mostly on dispersion forces or weak electrostatic forces (dipoles and quadrupoles), which are not stronger than the intertube forces in a bundle. At the same time, they do not form persistent associated and/or solvated structures to yield an ordered molecular arrangement of some kind with the nanotubes. Water does not disperse carbon nanotubes because it does not interact strongly with the

nanotube surface, even though it might be able to form ordered liquid structures due to its relatively strong hydrogen bonding capabilities. In order for a molecule to physically interact with the nanotube surface, it should contain π bonds to form π stacks (Chen et al. 2001), and/or it should be able to form a molecular complex, also called a π-complex (Morrison and Boyd 1983), with the nanotube surface. The latter situation happens when Lewis and protic acids are used. In terms of the formation of an ordered structure with carbon nanotubes, small molecules would have to be able to form associated structures (i.e., between like molecules) based, at least, on hydrogen bonding. If these associations between solvent molecules are based on anything less (such as dispersion or van der Waals forces), then the nanotube bundle can easily be separated into individual tubes.

The aspect ratio of carbon nanomaterials plays a critical role in their dispersion. The aspect ratio of a filament is the length divided by the diameter or width. Dispersing higher aspect ratio materials is easier due to a reduced interaction between potential agglomerates. These high aspect ratio carbons build viscosity, thus more shear, which aids in dispersion. Nanotubes/matrix compatibility also plays an important role in the dispersion. An improvement in wettability is usually accompanied by an improvement in dispersibility. The wettability improvement brought about by functionalization to the carbon in some systems usually enhances dispersibility. Dr. Banash of Zyvex discussed a new multifunctional surface treatment technology that optimizes the interaction between CNTs and the host matrix (Banash 2006). Zyvex's technology bridges functional groups onto the nanotubes, including ones that provide both excellent dispersion and adhesion to the matrix. Figures 3.2 and 3.3 illustrate the polyurethane/Kentera™ composite indicating an excellent dispersion and strong interaction with the host. Single nanotubes are easier to disperse than bundled or entangled nanotubes.
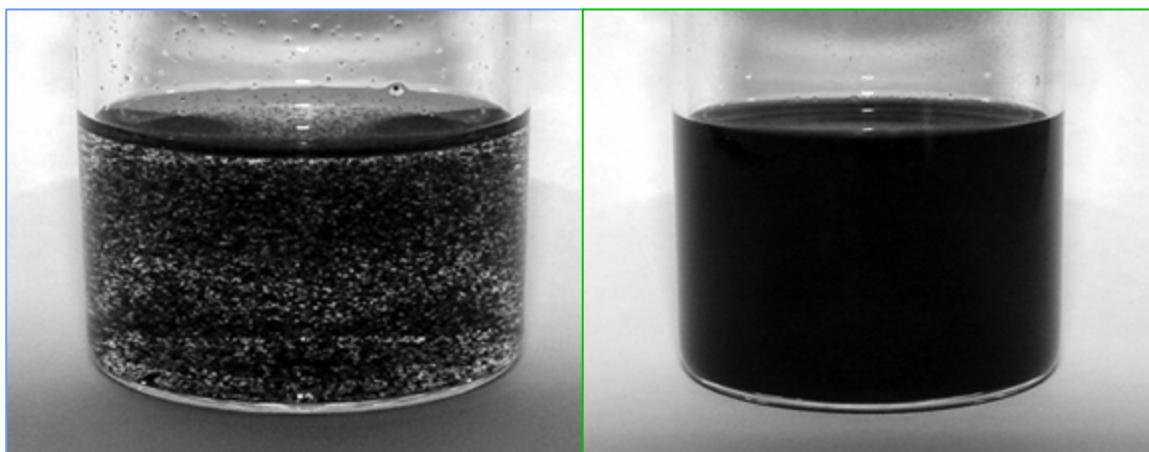
Figure 3.2. Example of poor (left) and good (right) dispersion of carbon nanomaterials in solution (Banash 2006, 142).

Figure 3.3. Example of poor (left) vs. good (right) dispersion of carbon nanomaterials in polyurethane films, and demonstration of stretching of well-dispersed CNT-polyurethane film (Banash 2006, 142).

Prof. D. Resasco from SouthWest Nanotechnologies (SWeNT) reported a stable dispersion of SWCNTs in surfactant solution derived from CoMoCat nanotubes (Figure 3.4) (Resasco 2006). Yuji Ozeki of Toray Industries also presented a method to completely disperse purified SWCNTs in ethanol solution; Toray's SWCNTs were synthesized by using alcohol as precursor and iron supported on zeolite (Ozeki 2006).
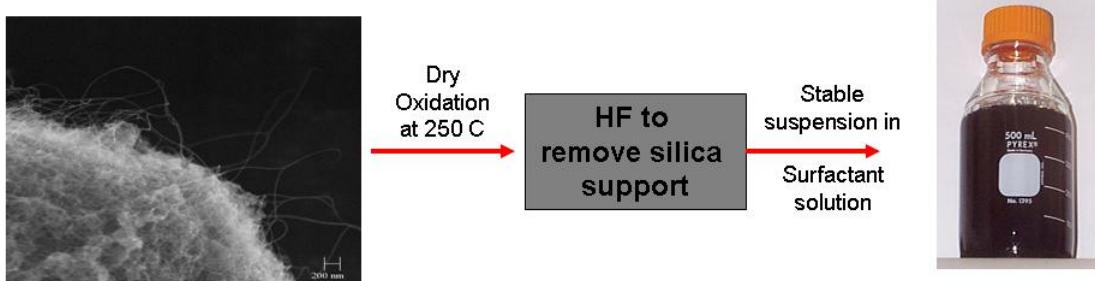
Figure 3.4. Process developed for dispersion of CoMoCat nanotube by SWNeT (Tan and Resasco 2005).

Within Japan, two groups have focused on mass production of CNT materials; both Nano CarbonTechnologies (a joint venture between Hodogaya Chemical Co., Ltd., and Mitsui Co., Ltd.) and Showa Denko have developed post-processing of CNT materials for specific applications, composites, and battery additives. The work of these groups stems from work originally pioneered by Prof. Morinubo Endo of Shinshu University. They used a floating catalyst CVD technique for production of different diameter carbon nanotubes. In addition, both groups have specialized in sophisticated post production techniques for improvement of the as-produced material and are using two steps of high-temperature thermal annealing up to 2200°C after growth in a CVD furnace. The thermal annealing process and the CVD furnace are reportedly incorporated as a single operating unit as opposed to being distinct processing steps. The flow chart below (Figure 3.5) indicates the production steps used. These groups claimed that the two-step thermal annealing and short tube length helps them in dispersing these carbon nanomaterials better in plastics, compared to nanotubes from other vendors (Figure 3.6).
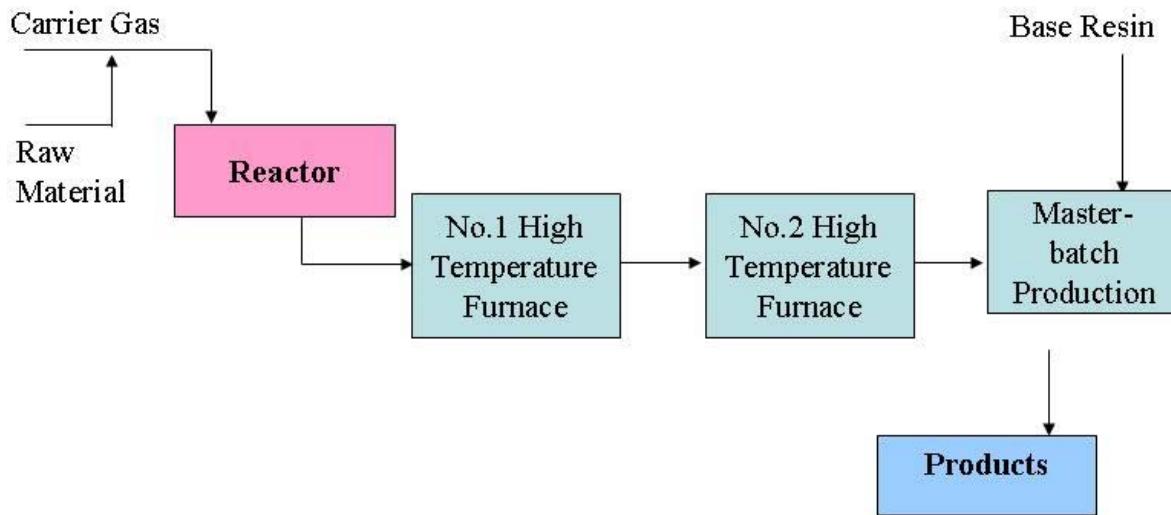
Figure 3.5.Schematic of floating catalyst CVD method.
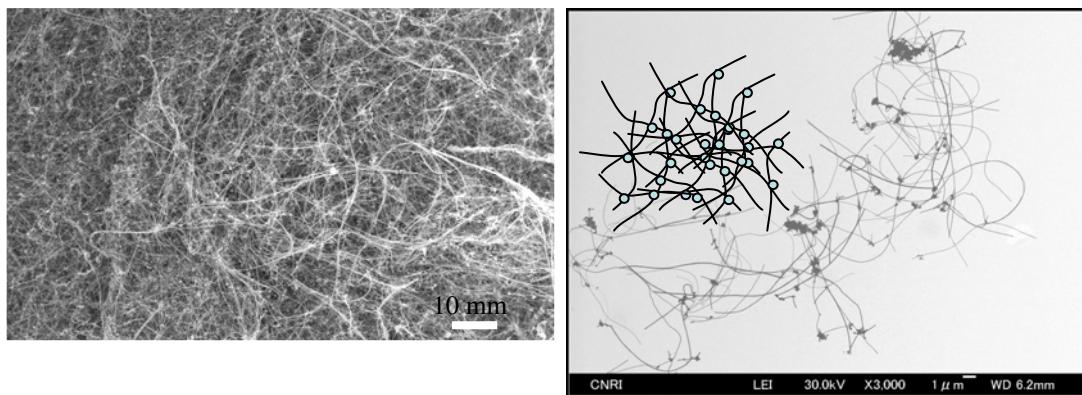
Figure 3.6. Microstructure of MWCNT materials produced by a continuous process at Nano Carbon Technologies Co., Ltd., Japan. SEM and TEM images of post-processed MWCNTS shown here. A TEM image was taken after dispersing the MWCNTs in toluene.

The first mass applications for MWCNTs are likely to be for protection against electrostatic discharge. For ESD applications, the electrical conductivity and high aspect ratio of MWCNTs are exploited to form an electrically percolating nanotube network at low loadings (a few wt %) within an otherwise high resistance plastic. This prevents static charge build-up on the surface of the plastic and constitutes a core business opportunity for Hyperion Catalysis International. Hyperion sells nanotubes premixed within thermoplastic master batch for ready-to-use formulations. These formulations have found use in the automotive industry in conductive nylon for fuel lines, connectors, and fuel filter housings, as well as in exterior plastic parts that must be conductive in order to permit their electrostatic spray painting. (Other ESD business opportunities exploited by Hyperion include clean room components where electrically-charged plastics degrade the environment by collecting dust, and plastic components used in the microelectronics industry — both in chip fabrication and in component packaging — which is increasingly sensitive to ESD-induced chip failures as insulating layers and channel lengths continue to shrink.) In Japan, Nano Carbon Technologies Co., Ltd., (NCT), is also selling post-processed nanotubes in master batch with thermoplastic and thermoset plastics for automobile applications similar to that of Hyperion. Figure 3.7 shows a scanning electron microscope (SEM) image of a cross-section of 5% post-processed MWCNTs in polycarbonate. It shows a better dispersion of the MWCNTs in the polycarbonate matrix without any degradation of the tubes, clearly with improvement in the resin's mechanical physical properties. It is expected that this dispersion will provide uniform conductivity and minimal shrinkage during molding.

Electromagnetic interference shielding applications differ from ESD principally in that EMI shielding requires a significantly higher conductivity. This can be achieved by increased loading of MWCNTs within the composite matrix; however, at some loading fraction the mechanical properties of the composite are typically degraded. Another problem associated with high nanotube loading is the very large increase in the viscosity of the melts for thermoplastics or the polymer precursor for thermosetting compounds. This makes it more challenging for dispersion of carbon nanotubes in the matrix.

Good dispersion of individual nanotubes within the composite body is the key to achieving the highest electrical conductivity at low mass loading while minimizing degradation of (or potentially enhancing) mechanical properties. This relates to one benefit associated with poorly graphitized walls in CVD-grown MWCNTs. These defective MWCNTs are less subject to the van der Waals bonding that couple well-graphitized MWCNTs and SWCNTs. The highly defective side-walls of CVD-grown MWCNTs also provide reactive sites for functionalization with groups meant to further facilitate dispersion.
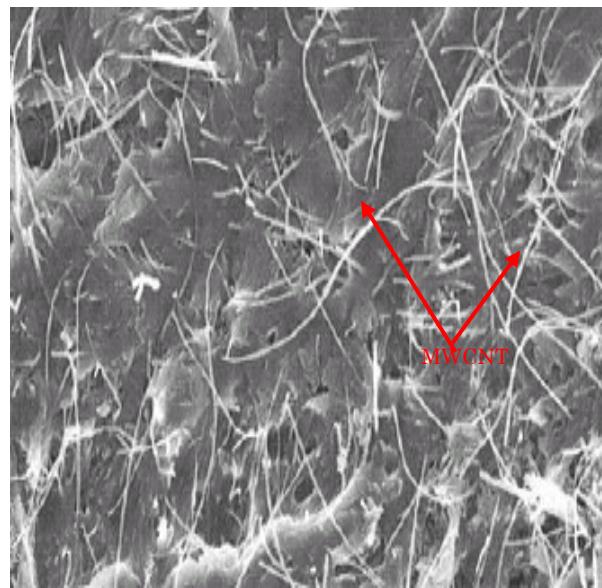
Figure 3.7. SEM image of cross-section of 5% MWCNTs in polycarbonate matrix (courtesy of Nano Carbon Technologies Co, Ltd., Japan).

Potential ESD and EMI applications for MWCNTs remain a common research theme in the United States, Japan, and China. For example, Prof. Wei Fei's group at the Department of Chemical Engineering of Tsinghua University has provided data on its mass-produced, CVD-grown MWCNTs in PET (polyethylene terephthalate), PET fibers, and PEEK (polyetheretherketone) polymers loaded with 0.1-1.6 wt% CNTs. The group claims excellent dispersion and electrical properties but a degradation in tensile strength. Although the present cost of SWCNTs makes them prohibitive for commercially competitive ESD and EMI applications, they have been explored by researchers in anticipation of eventual price reductions. Prof. Yongsheng Chen of Nankai University has provided information on the EMI performance of SWCNTs in epoxy composites. Measurements indicated a percolation threshold in epoxy of 0.062 wt% SWCNTs, attributed to a very good dispersion of the SWCNTs within the epoxy matrix (Figure 3.8).
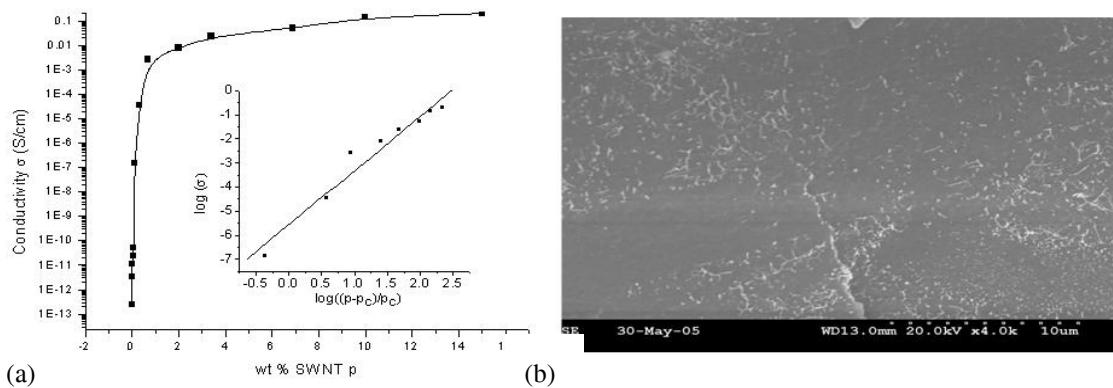
Figure 3.8. (a) Electrical percolation in SWNT-polymer composites, reached at 0.062% of "long" CNTs made by arc discharge using a Ni/Y catalyst; (b) SEM image of the cross-section of SWCNTs-long/ epoxy composite with 10 wt% loading (SWCNTs homogenously disperse composite) (Patel, Shuxi, and Yen 2006).

FUNCTIONALIZATION

Pristine nanotubes are unfortunately insoluble in many liquids such as water, polymer resins, and most solvents. Thus they are difficult to disperse evenly in a liquid matrix such as epoxies and other polymers. This complicates efforts to use the nanotubes' outstanding physical properties in the manufacture of composite materials, as well as in other practical applications that require preparation of uniform mixtures of CNTs with many different organic, inorganic, and polymeric materials.

To make nanotubes more easily dispersible in liquids, it is necessary to physically or chemically attach certain molecules, or functional groups, to their smooth side-walls without significantly changing the nanotubes' desirable properties. This process is called functionalization. The production of robust composite materials requires strong covalent chemical bonding between the filler particles and the polymer matrix, rather than the much weaker van der Waals physical bonds that occur if the CNTs are not properly functionalized. In many applications it is necessary to tailor the chemical nature of the nanotubes in order to take advantage of their unique properties. In the area of material chemistry, for example, problems such as phase separation, aggregation, poor dispersion within a matrix, and poor adhesion to the host must be solved. Dr. Banash of Zyvex has demonstrated that these problems can be solved by a new multifunctional surface treatment technology that optimizes the interaction between CNTs and the host matrix (www.zyvex.com). Zvex successfully tested this technology in all carbon nanomaterials, e.g., SWCNTS, MWCNTs, and carbon nanofibers (CNFs). Functionality may be customized to improve the dispersion and adhesion of nanotubes in polymer matrix, liquid systems, and others (Figure 3.9).
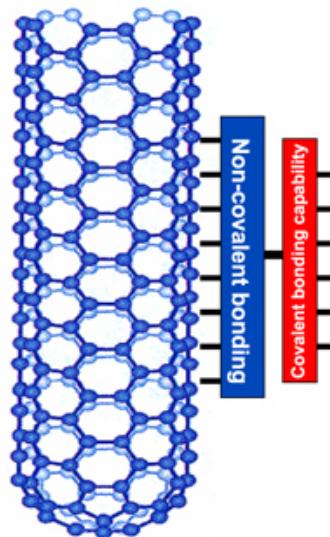
Figure 3.9. Zyvex's functionalization technology (Banash 2006, 139).

Prof. Barrera (2006) reported results of tests on a nanotube-epoxy polymer composite system with direct chemical bonding between the matrix and the functionalized SWCNTs. The terminal amino groups of the functionality covalently attached to the nanotubes can readily react with the epoxy and act as curing agents for the epoxy matrix, while bifunctional epoxy continues to react with the added diamine curing agents. Due to multiple amino groups attached to the SWCNTs, the resulting composites form a heavily cross-linked structure with a covalent bond between the nanotubes and epoxy matrix. Ultimately, the nanotubes were reported to chemically bond to the matrix and become an integral part of the composite, as shown in Figure 3.10. This method can also be extended to other polymeric systems to disperse carbon nanotubes properly.
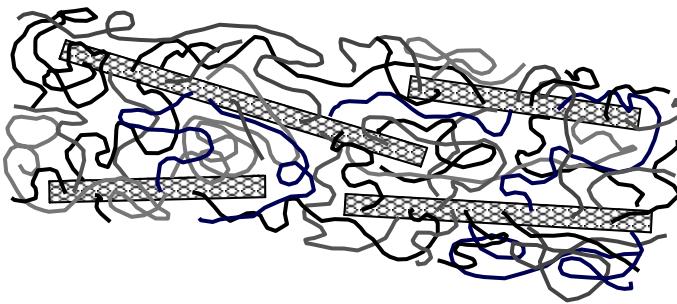
Figure. 3.10. Integration of the nanotubes into the polymer cross-linked structure (Barrera 2004).

Dr. B. Simard of NRC, Canada, emphasized the chemistry of reduced SWNT, rather than neutrals, because they de-bundle naturally, and this enhances the dispersion of SWCNTs in the matrix (plastic or in liquid) SWCNTs (Simard 2006). The overall time required for functionalization by this route was significantly reduced (minutes compared to several hours). He also proposed that the overall cost of functionalization is more cost-effective in comparison to other processes.

SWCNTs for Chemical and Biochemical Sensors

SWCNTs are ideal candidates for chemical and biochemical sensing. They greatly enhance electron transfer when used as electrode materials in electrochemical reactions. Cyclic voltammetric behavior of SWNT films functionalized with carboxylic acid groups has been studied; the SWNT-modified electrode showed highly electrolcatalytic behavior toward several biomolecules (Li et al. 2006). Also, the surface area of SWCNTs was reported to immobilize probe molecules with high density via either covalent bonding or van der Waals interaction.

According to Prof. Yongsheng Chen, Nankai University, nanoscale hybridization adducts of ferrocene (Fc) and SWCNTs were prepared and show high stability and greatly enhanced sensitivity toward hydrogen peroxide reduction (Chen et al. 2006). The electrochemical and hydrolysis results suggest that the strong π–π stacking interaction between Fc and SWCNTs play a critical role for its enhanced electrochemical catalytic property. The combined advantages from SWCNTs, Fc, and the cooperative effect due to this π–π stacking could make this adduct an excellent choice for ultrasensitive electrochemical detection. Prof. Chen reported that the SWCNTs used were prepared by the arc-discharge method and purified using nitric acid. The functionalization reaction was processed by suspending purified SWCNTs (1 mg) and Fc (20 mM) in a mixture (10 mL) of water and dimethylformamide (DMF) (1:4). The reaction mixture was mechanically agitated and immersed in a laboratory sonication bath, alternatively, at room temperature for 4 days. The hybridization adduct (Fc–SWCNTs) was collected with centrifugation and washed thoroughly by several sonication and centrifugation cycles using DMF. Figure 3.11 shows typical TEM and photo images and the corresponding EDS data for the purified SWCNTs and SWCNTs hybridization adduct with Fc, showing clear and numerous Fc assembling on the surface of the SWCNT bundles (Chen et al. 2006). The congregated particles of Fc were about 1.2–2.5 nm. The yellowish-black-colored transparent solution of Fc–SWCNTs strongly suggests that Fc is immobilized on the surface of the SWCNTs, and this immobilization also makes the SWCNTs more soluble in organic solvents such as DMF. Similar observations have been reported for other aromatic systems, such as porphyrin. The presence of the expected iron in the adduct structures was also confirmed by energy dispersive spectrometry (EDS) spectra with 4.9 wt% Fe in Fc–SWCNTs.
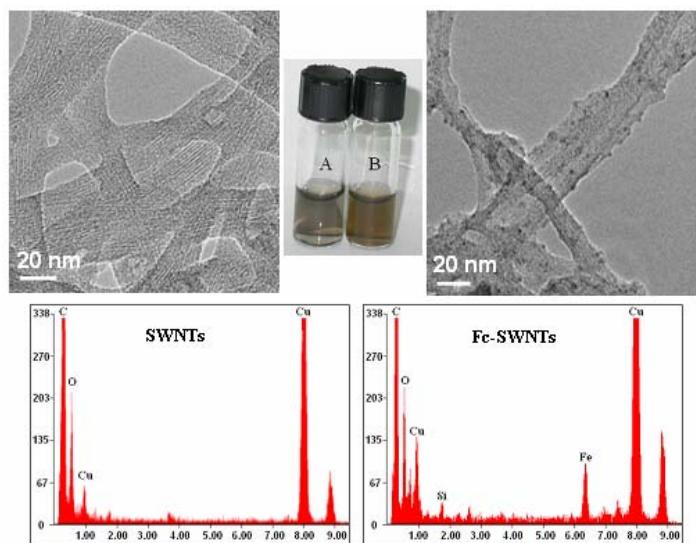
Figure 3.11. TEM images with EDS for purified SWCNTs (left) and Fc–SWCNTs adduct (right); (a) purified SWNT solely; (b) Fc–SWCNTs in DMF (Chen et al. 2006).

OBSERVATIONS

During this WTEC study, progress in dispersion of carbon nanotubes was observed in sporting goods and ESD and EMI applications in North America, Japan, and China. Zyvex, in partnership with a sporting goods company (www.eastonsports.com), is pushing these products for commercialization in North America. Prof. Endo of Shinshu University in Japan has suggested that MWCNT composites lead to an improvement in the performance of sporting goods. WTEC panelists have seen evidence suggesting the improvement in the performance of CNT composites for ESD or EMI.

More work is needed on dispersion, functionalization, and blending of SWCNTs to capitalize on the full potential of this unique carbon nanomaterial. Furthermore, more work is needed to scale up the purification of SWCNTs.

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CHAPTER 4

ORDERED ARRAYS OF CARBON NANOTUBES

Apparao M. Rao

BACKGROUND

Carbon nanotubes are well known for their unique physical properties, which depend sensitively on the dimensions of the nanotube. It is imperative to develop methods for positioning, orienting, and controlling the chirality and length of CNTs before they can be used in a broad range of applications. One approach, which involves the chemical vapor deposition of hydrocarbons in the presence of catalytic nanoparticles, has worked well and forms the basis for advances discussed in this chapter. Importantly, the CVD approach is amenable for scaled-up manufacturing of CNTs, and it is fully compliant with existing semiconductor processes for the development of CNT-based devices.

This chapter focuses on the synthesis of ordered MWCNTs and SWNTs. A few promising applications that are expected to impact emerging technologies are also discussed. The discovery of the electric-arc (Journet et al. 1997) and pulsed laser vaporization (Thess et al. 1996) methods for bulk production of CNTs has facilitated an in-depth understanding of the fundamental properties of CNTs and numerous applications that exploit the unique properties of CNTs (Dresselhaus, Dresselhaus, and Avouris 2001). However, several drawbacks exist with these bulk growth methods, such as the presence of amorphous nanosized carbonaceous materials, CNTs with a wide range of chiralities (how the graphene sheet rolls up into a tubular form), and randomly oriented bundles or ropes in the sample.

The growth of CNT arrays using a chemical vapor deposition of hydrocarbon precursors in the presence of nanosized transition metal catalysts has helped resolve some of these drawbacks. Arrays of high-quality MWCNTs were prepared from a catalytic decomposition of hydrocarbons on SiO_2-coated silicon and quartz substrates at temperatures that are relatively low (~700°C) compared to those used in the electric-arc or the pulsed laser vaporization methods (Figure 4.1) (Fan et al. 1999; Ren et al. 1998).
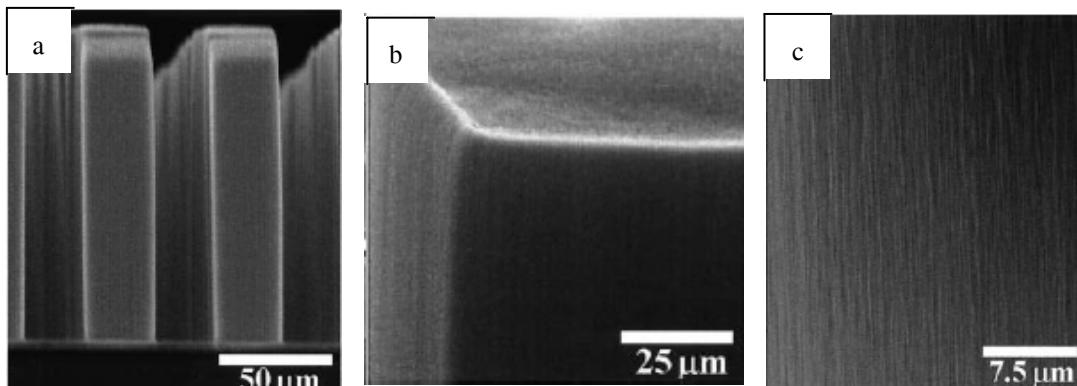
Figure 4.1. (a) SEM images of self-oriented MWCNT towers synthesized on silicon substrates; (b) SEM images showing sharp edges and corners at the top of a nanotube tower; (c) well-aligned MWCNTs in the direction perpendicular to the substrate surface (Adapted from Ren et al. 1998).

CNTs possess remarkable physical properties, however because of their size, they are difficult to manipulate or orient into ordered macroscopic structures for investigating their inherent anisotropic fundamental properties. Due the oriented nature of MWCNTs present in the CVD grown samples, initial studies focused on uncovering the anisotropic optical (Rao et al. 2000) and electrical transport properties (Wang et al. 2001) of MWCNTs. Subsequently, MWCNT arrays grown on large-scale surfaces served as scaled-up functional devices for use as scanning probes and sensors (Service 1998) and as field emitters (Saito et al. 1998). These advances motivated improved growth methods for CNT arrays and the plasma-enhanced CVD method (Ren et al. 1998), and enabled nanotube growth at lower (~450–500°C) growth temperatures with a high degree of control in the placement of CNT arrays on the substrate, and the overall dimensions of the array (Figure 4.2).

(a)   (b)
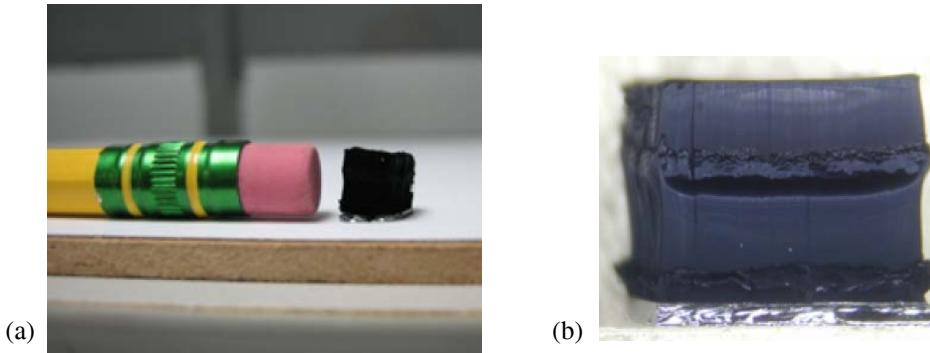
Figure 4.2. (a) Vesselin Shanov and coworkers at University of Cincinnati's Smart Materials Nanotechnology Laboratory used plasma-enhanced CVD to grow 7 mm tall MWCNT arrays on Si substrates; (b) an expanded view of the as-grown MWCNT array image (Ren et al. 1998).

While most of the university-based research has focused on the small-scale growth, characterization, and applications of MWCNT arrays, the Japanese industrial giant Fujitsu focused on the synthesis of large-area, oriented MWCNT arrays on Si substrates since it envisioned the likelihood of achieving dramatic improvements in interconnect technology based on oriented CNTs (Figure 4.3). As the size of electronic devices continues to shrink, the electronic industry is faced with several challenging problems that warrant a concerted R&D effort. For example, there is a growing demand for interconnects that can tolerate high current densities and simultaneously be impervious to electromigration.
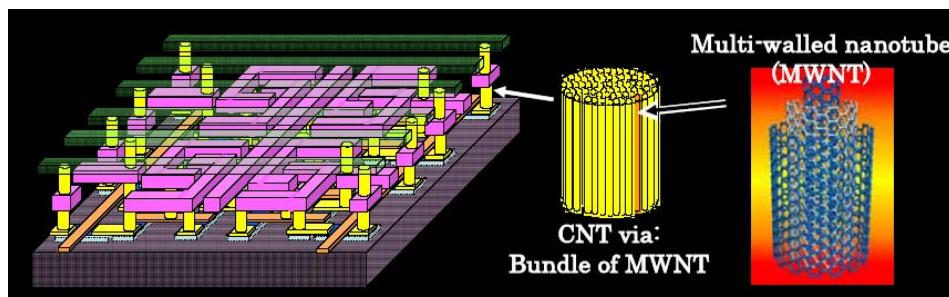
Figure 4.3. A schematic of Fujitsu's vision for integrating vertically aligned MWCNTs as vias for large-scale integrated circuits.

Copper interconnects have proved beneficial, as compared to Al interconnects; a current density of 10^6 A/cm^2 has been achieved. MWCNTs are being explored to push these limits even further; they could serve as very narrow interconnects with a current density approaching 10^9 A/cm^2. In addition to serving as heat sinks, the strong covalent bonds in the MWCNT minimize electromigration, thus providing a solid proof-of-concept for futuristic interconnects. Horizontal interconnects join field effect transistors together in different parts of an integrated circuit. Several layers of horizontal interconnects may be present, and each layer is separated by an inter-level dielectric. The overall assembly is thermally unstable above ~500°C. Vertical interconnects, called vias, pass through holes in the dielectric to join horizontal interconnects to the source, drain, or gate electrodes of an FET.

In December 2005, the Fujitsu team announced that it had developed the world's first CNT-based heat sink for semiconductor chips (Figure 4.4). These heat sinks dissipated large amounts of heat generated by high-frequency, high-power amplifiers; the nanotubes formed the bumps in a "flip-chip" structure. Fujitsu hopes to commercialize this heat sink technology within two years and to deploy it in base stations for next-generation mobile communications in about three years. The Fujitsu team has also developed CNT vias for large-scale integrated circuit (LSI) interconnects for 32 nm chips and beyond. Fujitsu hopes to commercialize its CNT-based interconnect technologies by 2012 (Figure 4.5).
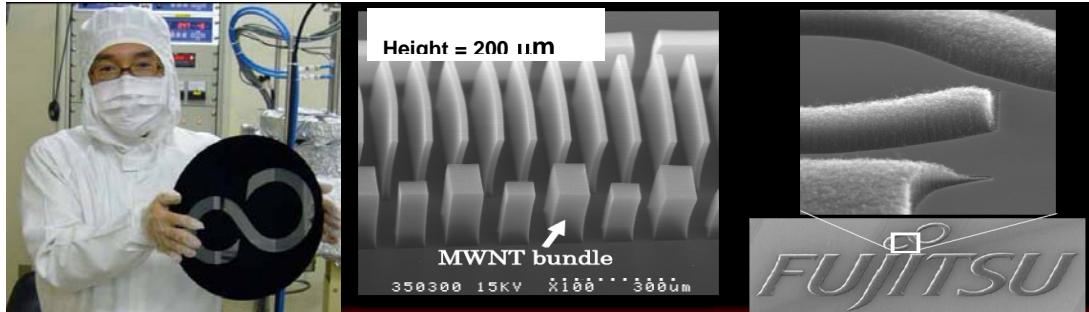
Figure 4.4. Large-area oriented MWCNTs prepared using Fujitu's low-temperature growth process involving hot filament/dc plasma CVD method and Ni and Co catalysts; controlled growth of MWCNT arrays is exemplified on the right.
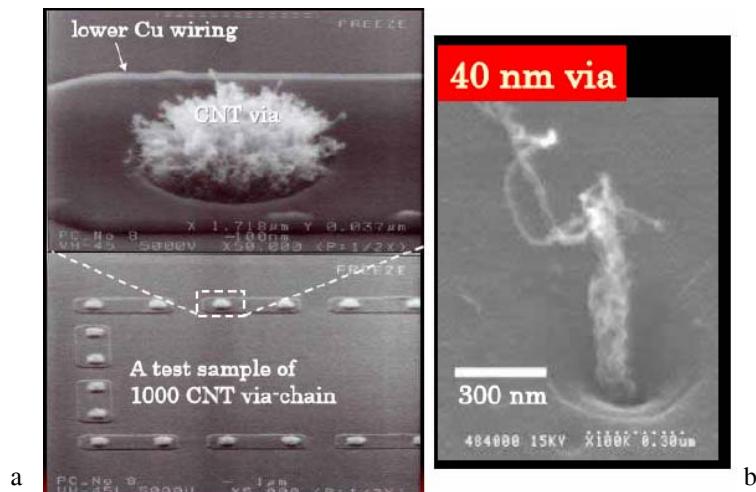
Figure 4.5. Interconnects for LSI are one of the target applications in Fujitsu's nano technology program. SEM images of a CNT via – chain fabricated at Fujitsu; (a) the via diameter can be tuned between ~1 μm to (b) ~40 nm.

Research in the CVD growth of CNTs is witnessing several rapid developments. Dr. Hata's group at Japan's National Institute of Advanced Industrial Science and Technology (AIST) laboratory has recently reported a water-assisted thermal CVD method for preparing high quality SWNT arrays (Hata et al. 2004).

The group members refer to their process as the "super growth method." It appears to result in a very efficient growth of vertically aligned single-walled nanotube forests (Figure 4.6), with heights up to 2.5 mm and carbon purity exceeding 99%. The super growth method is projected to address many critical problems such as scalability, purity, cost, and realistic applications involving CNTs. It is not clear yet that their tubes have a high degree of order in the tube wall.
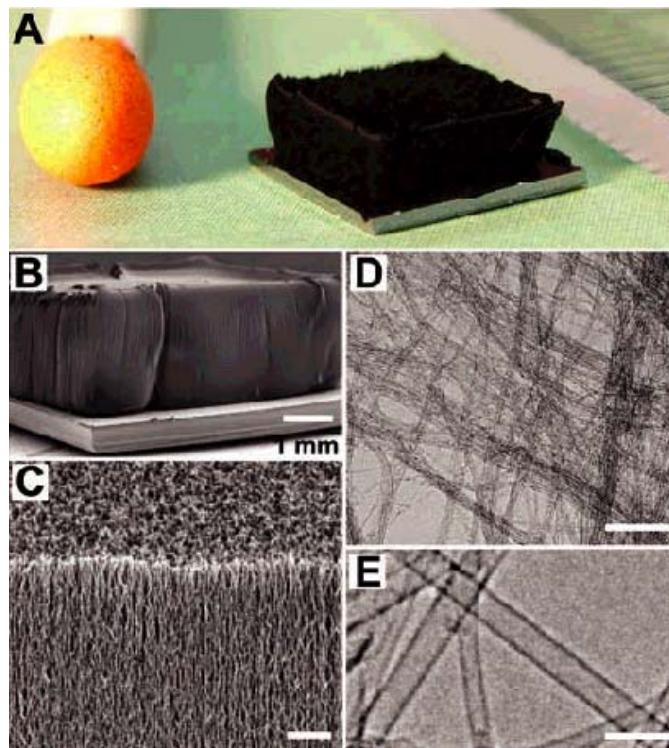
Figure 4.6. Oriented arrays of SWCNTs prepared using the super growth method. The height of the array is comparable to the size of match-stick head shown in panel (a). Subsequent panels show expanded views of the SWCNTs present in the array. The scale bars in panels (b) through (e) correspond respectively to 1 μm, 100 nm, and 5 nm (Hata et al. 2004).

One of the biggest challenges is controlling the physical dimensions of CNTs, as their electrical properties vary depending on length, diameter, and chirality. Controlling chirality is by far the most daunting task, and is viewed as the "Holy Grail" of CNT production. To date, bulk production of mono-chiral isolated SWCNTs has eluded researchers. Recently, Resasco's group at the University of Oklahoma successfully prepared SWNT bundles that predominantly contained chiral SWCNTs (Rao 2000, Ren 1998, Wang 2001, Tan and Resasco 2005). Bimetallic Co/Mo catalyst particles served as the catalyst and reproducibly favored the growth of SWCNTs with chiralities (Rao et al. 2000; Ren et al. 1998; Wang et al. 2001). SWCNTs produced by the electric-arc, pulsed laser vaporization (PLV) or the high-pressured CO conversion (HiPCo) methods do not exhibit any selectivity for specific tube chirality.

A leading fiber and textile manufacturer, Toray Industries, Inc., in Japan, has moved closer to realizing the Holy Grail of CNT production. Toray has developed a low-cost method for producing SWCNT and double-walled carbon nanotubes. Its method is based on thermal decomposition of hydrocarbons in the presence of iron catalyst particles in a temperature range 600–900°C. The dimensions of the catalyst particles are determined by the size of the pores present in the zeolites catalyst support (Figure 4.7). The tight catalyst particle diameter distribution presumably leads to a highly selective tube diameter and chirality distribution. Because of the well-defined size of the catalyst particles, Toray's method is conducive to producing high-quality isolated SWCNTs with well-defined chirality. Presently, the company produces and sells SWCNTs and DWCNTs in bulk quantities.
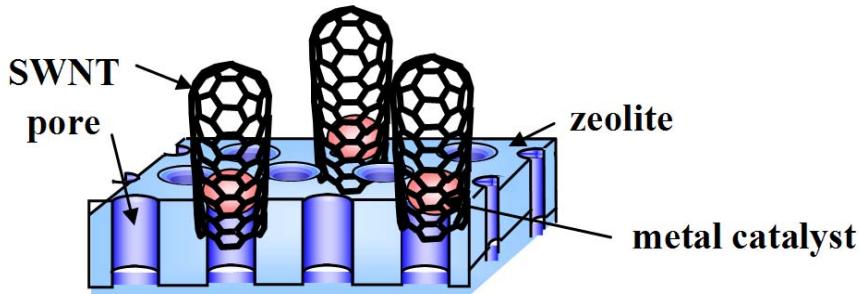
Figure 4.7. A schematic of the template-assisted CVD process developed by Toray Industries, Japan.

Much effort has also been expended in developing CVD methods for growing horizontally oriented MWCNTs on Si substrates (Wei et al. 2003). The results show that vertical and horizontal CNTs can be obtained by manipulating the electric field applied on the substrate and the flow direction of the gases. Recently, Liu and coworkers reported a "fast heating" CVD method that promotes the growth of long and aligned SWCNTs (Huang et al. 2004). They discovered that the rate at which the substrate temperature is ramped during the initial stages of the CVD process leads to the horizontally aligned SWNT arrays depicted in Figure 4.8. Figure 4.8a displays oriented and long SWNT arrays obtained by the "fast-heating" growth process (Huang et al. 2004); the Fe/Mo catalyst nanoparticles are deposited using photolithography, or by a simple deposition process. A mixture of CO/H_2 feed was decomposed at 900°C for 10 minutes to yield the SWNT arrays shown in the image. The right-pointing arrow at the top right corner indicates the direction of gas flow during the nanotube growth. Inset shows a portion of the sample on an expanded scale. Figure 4.8b shows a SEM image of SWNT array that cross over the etched trenches in the Si substrates.

A mechanism dubbed as the "kite-mechanism" has been attributed for the horizontal growth of SWCNTs. Compared with conventional CVD methods, the feed gas, catalysts, and many other experimental parameters in the "fast-heating" CVD are similar. The only major difference between these two methods is the heating rate of the substrate at the initial stage of the growth process (Huang et al. 2004).
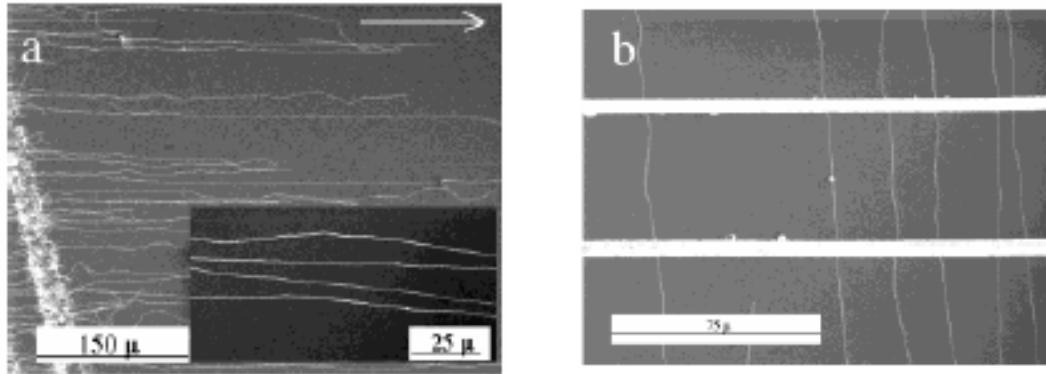
Figure 4.8. SEM images of individual SWCNTs prepared on an oxidized Si surface.

SUMMARY

The CVD method for nanotube growth is paving the way toward selective growth of particular chirality CNTs. Significant advances in the manufacturing of carbon nanotubes with controlled dimensions, and their placement at desired locations with desired orientations, have been achieved. Presently, we are witnessing these advances fuel on a global basis a clear transition in nanotube manufacturing from university bench-top growth chambers to industrial-scale pilot-plants. Very soon, we may overcome the barriers predicted by the legendary Moore's law without upsetting Rock's law (which is viewed as the economic flipside to Moore's Law), if present and future technologies stay focused on ushering in a new era of electronics by integrating CNTs with silicon technology.

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CHAPTER 5

MECHANICAL APPLICATIONS OF CARBON NANOTUBES

Pulickel M. Ajayan

BACKGROUND

One of the most promising bulk applications of carbon nanotubes is related to its place in composite materials based on the remarkable mechanical properties of nanotubes. From the early stages of nanotube discovery and development, there has been talk about nanotubes replacing carbon fibers in some form or other. However, this particular application of nanotubes in composites has been challenging due to various fundamental reasons, such as processing. Nevertheless, some applications based on mechanical properties are being realized in Japan and elsewhere using multi-walled nanotubes. This chapter will look at how the mechanical-property-based applications of nanotubes are emerging slowly into the marketplace and what the major challenges are, as well as what future prospects exist in this area.

MECHANICAL PROPERTIES OF CARBON NANOTUBES

The mechanical behavior of carbon nanotubes is exciting; nanotubes are generally considered to be the "ultimate" carbon fiber (Ajayan and Zhou 2001). The reason for this lies in the structure of nanotubes. In contrast to carbon fibers, the graphite "planes" are perfectly oriented along the fiber axis in a nanotube, giving all the amazing properties of the graphene sheet along the tube axis. Traditional carbon fibers have very high specific strength (strength/density) exceeding the strength of materials such as steel; moreover, the specific strength of nanotubes is even higher. From this perspective, if properly implemented, nanotubes should be excellent filler material in composites. Theoretical work and recent experiments on individual nanotubes have confirmed that nanotubes are among the stiffest structures ever made. Since carbon-carbon covalent bonds are among the strongest in nature, nanotubes would ideally produce an exceedingly strong material. Experiments have suggested that individual nanotubes could have a Young's modulus as high as 1TPa (Treacy and Ebbesen 1996). The observed tensile strength of individual nanotubes could come close to a few 100GPa, far better than traditional carbon fibers. The fracture and deformation behavior of nanotubes is intriguing. Nanotubes can sustain large strains under compression. The reversibility of deformations such as buckling has been studied. Flexibility and compliance of nanotubes depends on the geometrical parameters of the tube, such as the number of layers that make up the nanotube walls. Such flexibility of nanotubes under mechanical loading is important for their potential application as nanoprobes and in electromechanical applications. In short, nanotubes, both single-walled and multi-walled, have intrinsically excellent mechanical characteristics: extremely high stiffness, very high strength, elasticity, flexibility (in bending) and a high aspect ration (> 1000, mainly arising from the small diameters). All of these characteristics make this material ideal for mechanical applications.

It is fair to consider some distinction between SWNT and MWCNT at this stage. Although the basic building units (graphene cylinders) are identical in both structures, there are differences arising due to the assembly, geometry, and dimensions. Multi-walled nanotubes are concentric cylinders arranged one around the other; hence, intrinsic properties such as resilience and compressive strength would be different compared to SWNT, since the inner layers reinforce the outer shell against buckling. Similarly when load is applied, it is important in the MWCNT to have the ends open so that all the layers of the tube are subjected to loading, not just the outer shell. A similar problem also arises in SWNT since the individual nanotubes are often found

bundled into ropes; exfoliation to completely separate individual nanotubes is a difficult task. So, often, the properties of nanotubes that can be harvested correspond to collective behavior of aggregates (bundles or SWNT or MWCNT), and this will not be the same as the intrinsic properties of individual nanotubes. MWCNTs are also larger in diameter (2–50 nm, typically) compared to the tiny SWNT (1–2 nm diameter). MWCNTs prepared by chemical vapor deposition also do not have the high degree of crystallinity (graphitization) for the individual layers as the near perfect shells of SWCNTs. Hence, when one considers the comparative advantage of different kinds of nanotubes, one has to be careful about what structure of the nanotubes is being considered (Table 5.1).

Table 5.1 Mechanical Properties of Different Materials for Comparison with Carbon Nanotubes

Material	Young's Modulus (GPa)	Tensile Strength (GPa)	Density (g cm^{-3})
SWNT/MWCNT	~1000	~100-200	~0.7-1.7
High tensile steel	210	1.3	7.8
Toray carbon fibers	230	3.5	1.75
Kevlar	60	3.6	1.44
Glass fibers	22	3.4	2.6

MECHANICAL APPLICATIONS OF CARBON NANOTUBES

Given the outstanding and versatile mechanical properties of carbon nanotubes, there have been speculations about several applications of nanotubes that make use of these properties. From the information gathered during this WTEC study, these applications can appropriately be divided into four categories. Of these, two applications are already commercially successful in Japan (mechanical stabilizer in Li-ion batteries and some composite applications). Mechanical applications may be the only real applications of nanotubes that exist today. Mechanical applications of nanotubes are also the real bulk applications for this material, and success in this area will pave the way for large-scale manufacturing of nanotube material. Based on the demand of MWCNT in batteries (as mechanical stabilizers) and composites, Japanese companies (Showa Denko, Mitsui) are scaling-up their manufacturing capacities to several hundred tons of material per year.

Advanced Composites (fillers)

–   Polymer, metal, and ceramic matrix composites for strength, toughness, and vibrational damping
–   Coatings (thin film composites)

Electromechanical Probes in MEMS Technologies

–   Scanning probe tips
–   Compliant interconnects
–   Contact brushes

Mechanical Stabilizers (additives)

–   Miscellaneous

CARBON NANOTUBES IN ADVANCED COMPOSITES

As briefly mentioned earlier, the combination of physical properties of nanotubes make them ideal filler material in composites. There has been some work done in the area of metal matrix as well as ceramic matrix composites with nanotube fillers, but the majority of the work to date has focused on polymer composites. This discussion will focus attention on this class, simply because near-term commercial usage seems most pertinent to polymer composites. It should be mentioned that metal matrix composites (MWCNT in metals such as Al, Cu, Ti) have been used to mold mechanical parts. The nanotubes (especially MWCNTs) in these

increase the strength and electrical conductivity and impart thermal stability to the composite, but the enhancements of properties by the addition of nanotubes have been far from significant. Some products based on metal-CNT composites have been in use in Japan. Similarly, nanotubes (SWCNTs and MWCNTs) have been added to ceramic materials (e.g., alumina) to enhance the fracture toughness of the ceramic material. Unfortunately, not much enhancement in the fracture toughness was observed in the system. One possible application that can be envisioned, if substantial improvements in fracture toughness can be obtained, is in body armor, where the addition of nanotubes in ceramics not only improves the fracture properties, but also provides a significant weight advantage. The challenge is in the processing to get good dispersion of nanotubes in the composite and good interfaces between nanotubes and matrix (Figure 5.1). Nanotube fillers differ in morphology and conformations compared to traditional carbon fibers because they remain highly flexible and also form easy entanglements during dispersion in the polymer matrix.
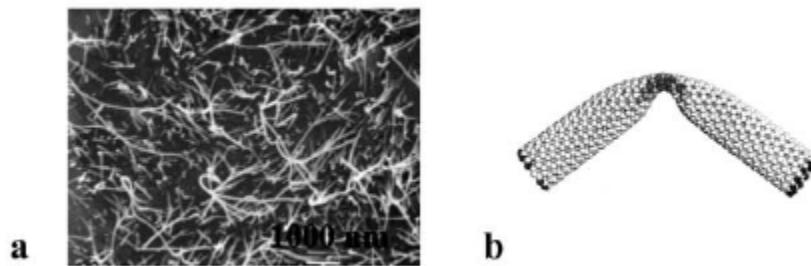
Figure 5.1. (a) SEM images showing typical dispersion of nanotubes (MWCNT shown here) inside a polymer matrix; (b) schematic showing the flexibility of nanotubes.

Carbon fibers have been used as reinforcements in lightweight, high-strength, high-performance composites; one can typically find these in a range of products ranging from expensive tennis rackets to spacecraft and aircraft body parts. Carbon nanotubes, the idealized carbon fiber in structure and properties, were touted to be the next generation of carbon fibers in terms of applications. Several groups, including NASA in the United States and traditional carbon fiber manufacturers such as Toray in Japan, have recently invested large amounts of resources in developing carbon nanotube-based composites for applications.

At first glance, nanotubes look extremely promising on several fronts: the intrinsically high modulus and mechanical strength, low density, and high interfacial area when incorporated into composites are advantages. Although nanotube-filled polymer composites have obvious advantages, there have not been many successful demonstrations that show significant advantages of using nanotubes as fillers over traditional carbon fibers. The main problems are creating a good interface between nanotubes and the polymer matrix and attaining good load transfer from the matrix to the nanotubes during loading.

There are two fundamental reasons for these problems. First, nanotubes are atomically smooth; unless properly engineered, the interface between nanotubes and the polymer matrix remains weak. Second, nanotubes are almost always organized into aggregates (as concentric arrangements in MWCNT and as bundles in SWNT), which behave differently in response to a load as compared to individual nanotubes. Earlier studies of load transfer using Raman spectroscopy suggested that by simply mixing nanotubes into a polymer does not guarantee good load transfer. Hence, recent approaches have all been based on chemically modifying the surface functionalities of nanotubes so that a good interface can be created. This is a challenging task, since the near-perfect structure of SWNT or highly graphitized MWCNT does not lend itself to easy alterations of surface chemistries (similar to oxidation-induced attachment of chemical functional groups on carbon fibers, termed "sizing"). For the CVD-grown MWCNT, the structure is more defective, and therefore, the chemical modification is easier. The recent successes in Japan on commercializing polymer composites with nanotubes have all been with CVD-grown MWCNTs. Table 5.2 shows a typical list of properties improved by adding MWCNTs (5% by weight) into polycarbonate (PC) matrix. Only marginal improvements are observed, and the situation is very similar for several other composites reported in the literature.

Table 5.2. Properties Improved by Adding MWCNT

PROPERTY	UNIT	NEAT PC	PC-MWCNT 5%
MWCNT Content	wt %	0.0	5.0
Tensile Strength	MPa	63.4	67.3
Tensile Modulus	GPa	2.4	3.8
Elongation	%	75.5	23.6
Flexural Strength	MPa	101	107
Flexural Modulus	GPa	2.4	3.0

Processing of nanotube composites has also been an issue. Due to the high surface area of nanotubes (in particular, of SWCNTs), mixing of polymers and nanotubes becomes an issue with respect to the increased viscosity of the mixture. In addition, complete exfoliation of the nanotube bundles during processing is never achieved (except in cases of low-loading and chemically-surface-modified nanotubes), leading to poor dispersion of nanotubes in the matrix. This has prevented nanotube-based composites from achieving the best mechanical properties that were hypothetically imagined. Nevertheless, using the inferior, CVD-grown nanotubes, reasonably good dispersion and loading of up to 10 wt% of nanotubes have been achieved. The first set of applications of these nanotube-based polymers (epoxy, several thermoplastics) has been in the area of sporting goods (Figure 5.2), and several companies in the United States (e.g. Zyvex, focusing on the use of SWNT) and Japan (Mistui, Toray, etc., using CVD-grown MWCNT nanotubes) are actively involved in pursuing these applications.

Figure 5.2. MWCNT-based polymer sporting goods.

The large application domain for carbon fibers, namely high-strength composites for aerospace, particularly 3D composites made from weaved carbon fiber stacks, has not been considered as a viable application for carbon nanotubes. The reason is the fact that nanotubes are still short in length (fits more the category of short fibers, which have only limited use in structural applications). There are several works that deal with continuous fibers spun from nanotubes, but unless these can be produced in relatively large quantities and with high degree of orientation of nanotubes in the fibers (so that the mechanical properties of these spun

fibers can compete with those of traditional carbon fibers), the option of using nanotubes in structural composites will remain a distant dream. Perhaps in the next several years, we will see an improvement in the properties of nanotube fibers that are spun using different techniques. However, nanotubes can aid in the improvement of 3D composites. The traditional fiber-reinforced composite materials have excellent in-plane properties, but properties of out-of-plane through-thickness fare poorly. There have been several approaches, particularly in new fiber packing designs, but all these have had only limited success. An approach to the 3D composite challenge, using nanotube incorporation without altering the 2D stack design, has been shown recently. This is on the basis of aligned interlaminar carbon-nanotube forests (CVD-grown) that would provide enhanced multifunctional properties along the thickness.

Direction

Carbon nanotube forests could allow the fastening of adjacent plies in a 3D composite. These nanotube forests provide much-needed interlaminar strength and toughness under various loading conditions. For the fabricated 3D composites with nanotube forests, remarkable improvements in the interlaminar fracture toughness, hardness, delamination resistance, in-plane mechanical properties, damping, and thermoelastic behavior was observed (Veedu et al. 2006). Figure 5.3 is a schematic diagram that shows how nanotubes could be incorporated into 3D fiber-laminae-reinforced polymer composites. Here, aligned arrays of MWCNT are CVD-grown on fiber cloths, stacked, and then infiltrated with polymer to fabricate the 3D composite. The nanotubes provide the fastening between individual fiber stacksimproving the through-thickness properties dramatically.
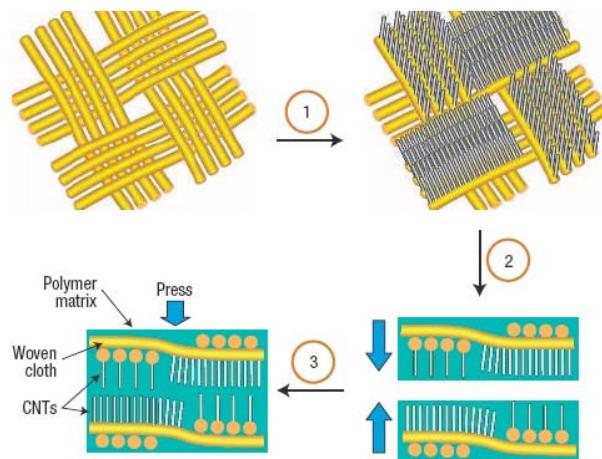
Figure 5.3. Nanotubes incorporated into 3D fiber-laminae-reinforced polymer composites.

In addition to strength and fracture toughness, there are other mechanical properties of structural composite materials that can be improved by addition of carbon nanotubes. In fact, the perceived weakness in nanotube-embedded composites, due to the lack of good interfaces, can be converted into useful applications, for example, vibration damping. A body of work done in recent years suggests that there is great potential in fabricating nanotube-filled polymer systems that can improve vibration damping by an order of magnitude when compared to pure polymeric materials (Suhr et al. 2005). Work has shown that the nanotube-matrix sliding energy dissipation mechanism can induce nearly three orders of magnitude increase in a loss modulus of a polymer matrix with relatively small (1-2%) weight fraction of well-dispersed (chemically functionalized) SWNT fillers. Impressive damping increases in epoxy resins have been reported with SWNT fillers.

 The work on the use of nanotube fillers to improve damping in polymers has now been taken up by industry (e.g., Boeing). If large-scale manufacturing of nanotube-based composites can be implemented in a scalable way, nanotube fillers as damping elements in composites could be a real bulk application for this material.

Finally, there are several other possibilities with nanotubes in polymers that could become viable applications in the future. Since the structures can be grown in an ordered fashion, they can be made into fibers and sheets

that allow the fabrication of thin film composites, as well as composite fibers. The creation of nanotube cables with highly aligned nanotubes in polymer fibers could lead to mechanically strong, highly conducting cables (Li, Kinloch, and Windle 2004). Similarly, thin film polymer composite coatings where the nanotubes are aligned in one direction could produce mechanical hardened polymer coatings with much better thermal stability. The combination of excellent mechanical, electrical, and thermal properties of nanotube fillers can be useful in a variety of products that can lead to multifunctional structures.

Electromechanical Probes in MEMS Technologies

The combination of excellent mechanical and electrical properties of nanotubes provides a strong case for applications in electromechanical devices. Conducting probes is one of these applications. The first commercial (albeit low-volume) application of nanotubes is indeed in this domain. With extremely small sizes, high conductivity, high mechanical strength, and excellent flexibility (ability to easily bend elastically), nanotubes, either as individuals or as organized arrays, can become indispensable in their use as nanoprobes (Dai et al. 1996). Use of a single MWCNT attached to the end of a scanning probe microscope tip for imaging has already been demonstrated. Today, the nanotube tip for scanning probe microscopy tools is a commercial product. The advantage of the nanotube tip is its slenderness and the possibility of image features (such as very small, deep surface cracks), which are almost impossible to probe using the larger, more blunt etched Si or metal tips. In addition, due to the high elasticity of the nanotubes, the tips do not suffer from crashes on contact with the substrates.

Electromechanical actuators have been constructed using sheets of nanotubes. It was shown that small voltages (a few volts), applied to strips of laminated (with a polymer) nanotube sheets suspended in an electrolyte, bends the sheet to large strains, mimicking the actuator mechanism present in natural muscles (Baughman et al. 1999). The nanotube actuators would be superior to conducting polymer-based devices. This interesting behavior of nanotube sheets in response to an applied voltage suggests several applications, including as nanotube-based micro-cantilevers for medical catheter applications and as novel substitutes, especially at higher temperatures, for ferroelectrics. These are, however, potential applications, and none has been commercialized yet.

Another interesting application for nanotubes is in the area of contacts. There is a lot of potential for nanotubes to be used as compliant, brush-like contacts. It has been shown recently that aligned arrays of nanotubes act as super-compressible foams, being able to undergo large numbers of compressive cycles, at high strains. The outstanding fatigue resistance and extraordinary soft-tissue-like behavior (showing visco-elastic behavior) indicate that properly engineered carbon nanotube structures could mimic artificial tissues, and their added high electrical conductivity could make them excellent candidates for use as compliant electrical contacts and interconnects in electromechanical systems and probe cards. Some of these electro-mechanical properties of nanotubes are beginning to be used in commercial systems and would find practical use in future technologies.

Application as Mechanical Stabilizer

Today, there are two important bulk applications for carbon nanotubes, both involving CVD-grown MWCNTs. One, the MWCNTs manufactured by Hyperion are used for ESD applications in polymers. The main industry that uses nanotubes here is the plastic manufacturer, in particular General Electric, using tonnage quantities of MWCNT mixed in with their structural plastics. This application is based on the high electrical conductivity of nanotubes and low percolation threshold due to their high aspect ratio. The second bulk application — electrodes of batteries — is based on the mechanical property of nanotubes. This application has been developed in Japan and feeds the battery electrodes of Sony batteries, especially the Li-ion cells. Two companies are involved in the large-scale manufacture (capacities reaching a few hundred tons/year) of MWCNTs to supply this application, Mitsui and Showa Denko, both of which use variations of the "Endo" process for manufacture of MWCNT.

Figure 5.4 shows the effect of larger MWCNTs (otherwise called VGCF, or vapor-grown carbon fiber) added to carbon electrodes in mechanically stabilizing the electrodes during long time charge-discharge cycles in a Li ion battery.
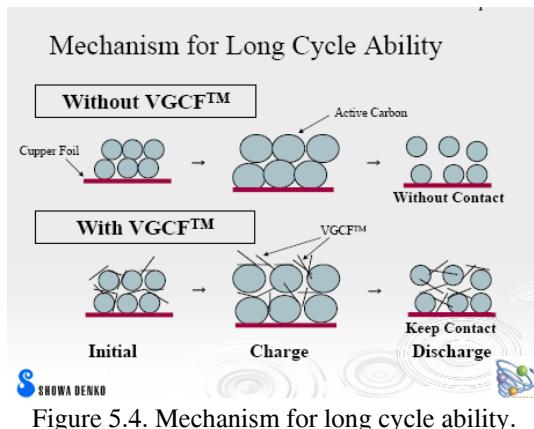
Figure 5.4. Mechanism for long cycle ability.

It has been known that the electrode in batteries, which is made of carbon (partially graphitic carbon), undergoes disintegration during the charge-discharge cycles of the battery operation. In Li ion batteries, since Li ions go in and out of the electrodes during charging and discharging, there occurs expansion and contraction of the electrode materials and hence, large amounts of stress. With only the partially graphitized carbon electrode, the microscale grains fall apart during these expansion/contraction cycles and finally lose contact with each other, decreasing electrochemical activity (significantly changing discharge capacity). With the MWCNTs in the electrodes (Figure 5.4), grains in the electrodes remain connected even after a large number of cycles because the nanotubes or fibers facilitate this connectivity. Addition of MWCNT/VGCF has been shown to significantly improve the number of charge/discharge cycles that the battery can withstand without any significant decrease of the discharge capacity (Figure 5.5) (Endo et al. 2001). The property of nanotubes that aids in this application is resilience (compared to other forms of graphitic carbon). It is expected that the volume demand for MWCNTs in this application will increase dramatically in the next several years. Carbon nanotubes have also been proposed as active electrode materials (where Li ion intercalation occurs in a way similar to graphite electrodes), and the combination of electrochemical properties and mechanical stabilizing effects could lead to valuable applications of nanotubes as electrode material.
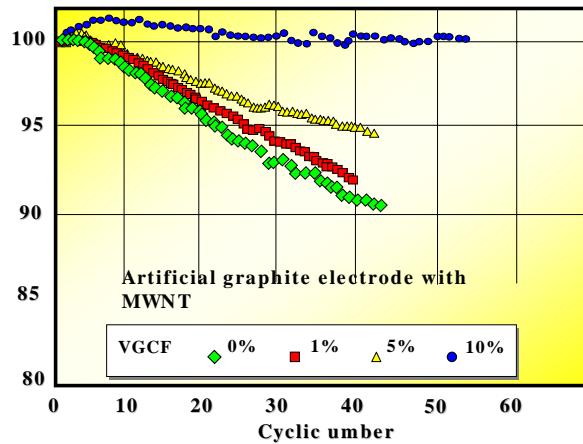
Figure 5.5. Cyclic characteristics of synthetic graphite anodes in Li-ion batteries as a function of weight percentage of MWCNT in the anode. The vertical-axis represents the percentof the initial discharge capacity (courtesy of Morinobu Endo).

Miscellaneous Applications

In addition to the applications mentioned above, there are several others based on what has been demonstrated in the laboratory in the last decade. Individual nanotubes are very stiff structures, and the use of these as cantilevers for sensing of gases adsorbed on these have been proposed. Several designs of actuators, membranes, and sensors based on individual nanotubes, as well as assembled nanotube structures, have been

discussed. With small dimensions and a combination of excellent mechanical and electrical properties, nanotubes could find their way into nanoelectromechanical systems. Regarding filler applications, in addition to the epoxy and thermoplastics that are commonly considered, elastomers filled with nanotubes have also been studied. In particular, where mechanical improvements and thermal stability can be achieved by incorporation of nanotubes in elastomers, there will be scope for applications. The use of nanotubes as tiny probes was already mentioned. An extension of this would be applications in bioengineering. Nanotube tips functionalized with biomolecules can be used in imaging, as well as in manipulation of a variety of biological species. There has even been report of using a pair of nanotube tips to function as tweezers for nano-manipulation. Polymer composites stiffened with nanotubes could provide the next generation of stents in biomedical implant applications. Microcatheters made from polymer (Nylon-12) nanotube composites have already been demonstrated (Endo et al. 2005); these provide better handling and blood-coagulation properties and higher stiffness compared to pure polymer. Organized nanotube structures can also provide new and fascinating avenues of applications. Arrays of nanotubes grown on microscale fibers can act as brushes (nanotube bristles) which can be useful in a variety of applications ranging from cleaning micro-trenches to contact brush-switches.

CHALLENGES AND FUTURE PROSPECTS

The mechanical applications of nanotubes will probably require the largest volume of nanotubes. Among these, fillers in polymer composites and mechanical stabilizers in batteries dominate the scene. The biggest challenge will be to figure out the right way to disperse the nanotubes in composite structures. It does not look promising for nanotubes to replace existing carbon fibers in structural applications where the fibers are the load carrying elements. Unless nanotube-based long fibers can be spun in a scalable manner, and these fibers challenge the mechanical properties of traditional carbon fibers, this will be a tough task. However, novel ways of incorporating nanotubes into the existing framework of composites would ensure large volume demand for nanotubes. Incorporation of nanotubes to improve through thickness properties of 3D composites, or introduction of dispersed nanotubes in polymer matrices to improve vibrational damping, are examples of this scenario. Nanotubes as matrix modifiers and solid state curing agents could allow the large-scale entry of nanotubes into polymer composite structural applications. In order to obtain high-strength polymer composites with nanotube fillers alone, we would need complex interfacial engineering, and it is not clear if this would be cost-effective or if this would provide significant enhancements in properties that would justify its use. For the time being, the largest bulk application seems to be the mechanical stabilizing effect of MWCNT in battery electrodes due to the excellent mechanical resiliency of these nanotubes.

Other major challenges in the mechanical applications of nanotubes concern bulk manufacturing and processing of the different types of nanotubes that are available. To date, MWCNTs seem to be winning the battle, particularly due to the fact that these are available today in large quantities, and also, certain properties of these structures (such as resiliency) have been found valuable for specific applications. SWNTs seem to be a more difficult material to work with from the perspective of manufacturability, processing (exfoliation of bundles), and interfacial properties. However, it needs to be remembered that SWNTs are a new material (compared to MWCNTs, which have been under development for over two decades) and clearly possess better properties compared to MWCNT. One could imagine that, ultimately, SWNTs would also find a role in the mechanical applications and become a strong player in the largest-volume application, which is the development of advanced composites based on polymers and nanotubes.

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CHAPTER 6

ELECTRONIC, OPTICAL, AND OPTOELECTRONIC APPLICATIONS OF CARBON NANOTUBES

A. John Hart, Andrew Rinzler, and Jing Kong

BACKGROUND

The exceptional properties of CNTs are motivating their use in numerous electronic, optical, and optoelectronic applications. These applications range from mixing of lightweight fractions of disordered multi-wall CNTs in polymers for enhancement of electrical conductivity and for electrostatic discharge, to ordered integration of individual single-wall CNTs on substrates for use as nanoelectronic and optoelectronic device elements. Each application within this spectrum places unique demands on CNT manufacturing operations in areas such as CNT quantity, purity, diameter and length distribution, and metallicity. This chapter gives an overview of the promises and challenges of applications of CNTs in electronics, outlines manufacturing and processing requirements for CNT electronics, and overviews state-of-the art techniques for meeting these applications. Example electronic applications are discussed, including transistors and oscillators, chemical sensors, interconnects emitters, memory, transparent conductors, batteries and supercapacitors, and conductive plastics. At present, large-scale manufacturing of high-quality MWCNTs primarily in Japan and the United States has enabled large-scale commercial use of CNTs in conductive plastics and lithium-ion batteries. Applications of CNTs in transparent conductors, interconnects, and memory appear to be market-ready within five years, while electronic and optoelectronic devices remain at the research stage.

PROMISES OF CNT ELECTRONICS

The promise of using CNTs in electronics lies in a set of favorable characteristics that are derived from their tubular graphitic structure, (ideally) low defect density, and high aspect ratio. The strong covalent carbon-carbon bonds in CNTs make them mechanically and chemically robust; they are able to withstand large electrostatic forces and are impervious to electromigration (capacity exceeding 10^9 A/cm$^{2)}$ (Dresselhaus, Dresselhaus, and Avouris 2001). The chirality of SWCNTs determines their electrical conductivity; by selecting their chirality, CNTs can be either semiconducting with a diameter-dependent band-gap, or metallic. Ballistic transport, where electrons travel through a CNT without scattering, has been demonstrated at micron length-scales for semiconducting SWCNTs (Javey, Guo, and Wang 2003) and metallic MWCNTs (Li et al. 2005). CNTs have high electron mobility and can be doped by charge transfer, and as direct band gap materials they can simultaneously exhibit electronic and optoelectronic functionalities.

The potential electronic applications of CNTs can be organized in terms of the complexity of the required arrangement of CNTs, as shown in Figure 6.1. For example, use of CNTs in plastics to achieve electrical conductivity requires bulk mixing of a large quantity (albeit a low volume fraction) of CNTs having low order; the CNTs must only form a loose network to alter the electrical properties of the matrix. On the other end of the curve, electronic devices using individual CNTs demand directed placement of these CNTs on substrates, with precise control of the CNT quality and electrical properties.

Applications mixing disordered CNTs in plastics and batteries were the first to be commercialized and now enjoy wide market penetration; applications in transparent conductors (which use tangled films of high-purity CNTs, ideally SWCNTs) are on the threshold of commercialization; applications in microelectronics, such as interconnects and transistors requiring highly-ordered CNTs and, in some cases, isolated SWCNTs of a particular conductivity, are still at the research stage. These "threshold and beyond" applications are limited by our ability to manufacture and/or process appropriate quantities of CNTs having necessary characteristics.
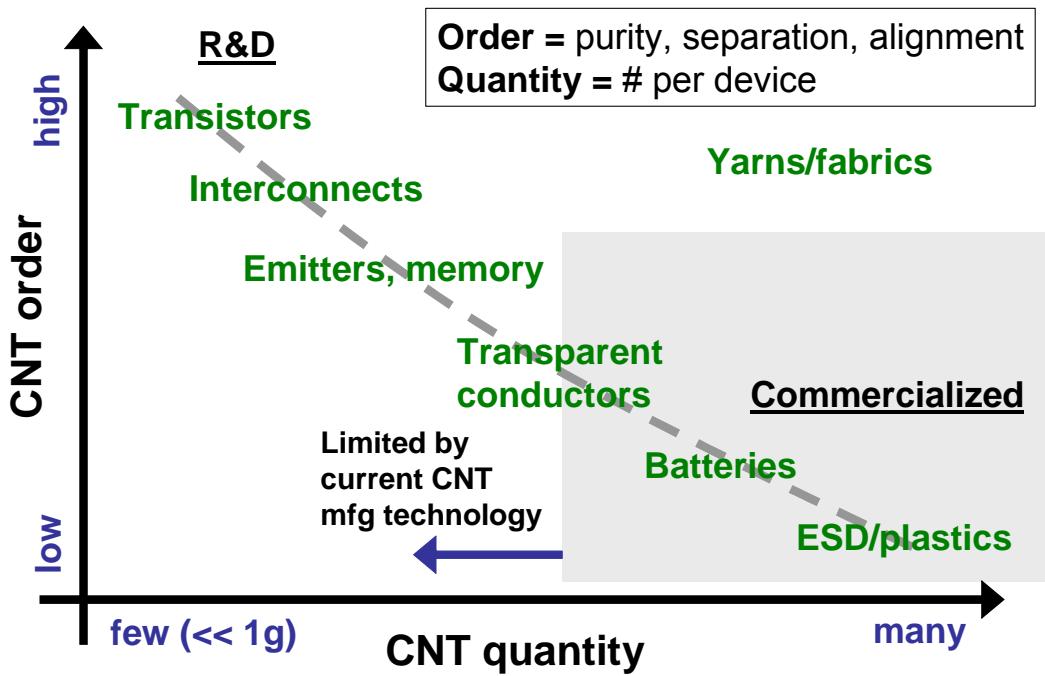
Figure 6.1. Map of prospective electronic applications of CNTs, relating each application area to the required complexity of CNT manufacturing and integration.

Table 6.1 lists major electronic, optical, and optoelectronic applications of CNTs. The sections that follow in this chapter describe the applications that the CNM panel found to be nearest to commercialization, as dictated by significant progress toward achieving application-oriented technical objectives and/or by recognition of significant near-term market potential in the particular area.

Table 6.1. Major Electrical, Optical, and Optoelectronic Applications of CNTs

Composites	- Electrostatic discharge (ESD) - Electromagnetic interference (EMI) - Radar absorption/reflection
Batteries and supercapacitors	- Electrodes - Additives
Fuel cells	- Electrodes - Catalyst support
Field-emission sources	- Displays - Single-tip electron guns (SEM, TEM electron sources) - Multi-tip electron guns for x-ray sources - Ion propulsion

Microelectronics	- Single-tube devices: field effect transistors (FETs), diodes, light emitters and detectors, oscillators, electromechanical resonators, oscillator balance - Nanotube networks/films: memory; thin film transistors (TFTs); transparent electrodes for organic light-emitting diodes (OLEDs), photovoltaics and electrochromics; saturable absorbers; neutral density filters; radar reflective windows; polarizers (aligned nanotubes); bolometers - Nanotube bundles: interconnect vias
Sensors	- Single nanotube FET configurations - Network configurations: impedance monitored TFT configuration; capacitance monitored; coatings for enhanced sensitivity/selectivity
Medical	- Photo-emissive glucose sensor - Cancer cell targeted radiation absorber - Electrophysiological probes - Cell scaffolds

ELECTRONICS-ORIENTED CNT MANUFACTURING AND MAJOR CHALLENGES

While the nested tubular structure of MWCNTs was first definitively identified in 1991 (Iijima 1991), it is now recognized that VGCFs, made purposefully for the first time in the 1970s (Oberlin, Endo, and Koyama 1976), were essentially what are now termed CVD-grown MWCNTs. Such VGCFs were first investigated for commercial applications in Japan by Showa Denko, and first commercialized in the United States as carbon fibrils by Hyperion Catalysis International in the 1980s. Given this much longer history, and the much lower cost of production, it should be no surprise that CVD-grown MWCNTs are also ahead in terms of commercialization.

Before proceeding further we should also note distinctions between MWCNTs in terms of the quality of their wall graphitization. The arc-grown MWCNTs discovered by Iijima in 1991 were grown without catalysts, forming under appropriate reactor conditions as a deposit on the cathode of the carbon arc apparatus. This process, when further optimized, yielded MWCNTs of the highest wall graphitization in which the nested cylindrical walls of the individual nanotube layers were virtually perfect, running parallel with each other for microns of tube length (Figure 6.2) (Ebbesen and Ajayan 1992). Because of slow MWCNT production rates and a need for oxidative purification that burns away the major fraction of the deposit, the carbon arc process for MWCNT production has not been scaled-up to industrial levels. CVD-grown MWCNTs, in contrast, possess far less well graphitized walls (Figure 6.3), with the degree of graphitization further differing greatly between different CVD processes.
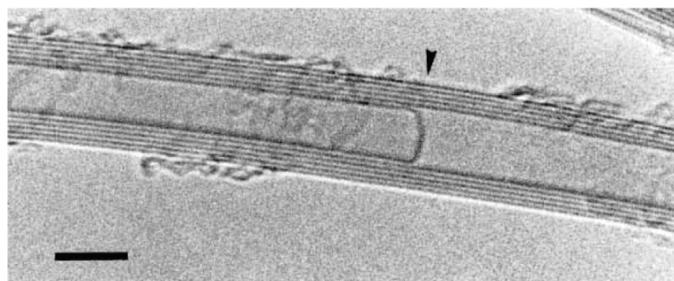
Figure 6.2. Arc-grown MWCNT showing the near perfect wall graphitization (arrow points to an internal closure).
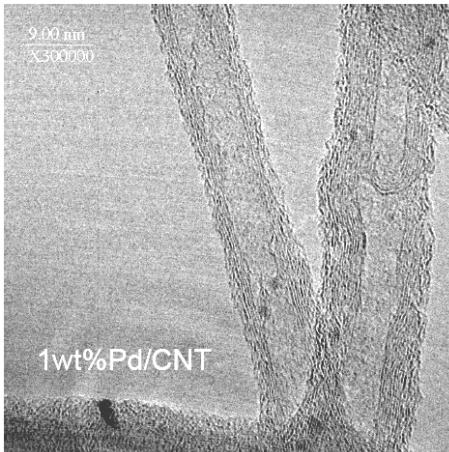
Figure 6.3. CVD-grown MWCNTs showing the disorder in the wall structure typical of MWCNT CVD synthesis. The MWCNTs here provide a catalyst support (small darker Pd particles).

Such lack of crystalline perfection degrades the intrinsic nanotube strength and electrical conductivity, which might be detrimental to certain applications; however, some applications can actually benefit. In cases where greater crystalline graphitization of the MWCNT sidewall is necessary for the application, high-temperature heat treatments (2600°C) are employed by companies like Showa Denko and Nano Carbon Technologies, Ltd. (Figure 6.4). However, such annealing adds significant manufacturing cost.
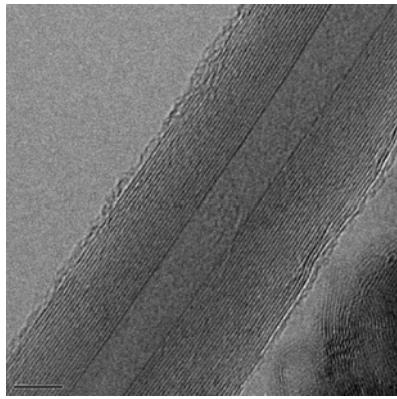
Figure 6.4. A CVD-synthesized MWCNT following a 2600°C
heat treatment to graphitize its walls.

While manufacturing of larger-diameter MWCNTs has been successfully scaled, much ongoing research and development effort focuses on the production of small-diameter MWCNTs, double-walled CNTs, and SWCNTs. The WTEC panel interacted with many companies working in this area, including Carbolex (U.S.; arc discharge process), Southwest Nanotechnologies (U.S.; CVD process), NRC/Simard (Canada; thermal plasma process), Iljin Nanotech (Korea; CVD process), and Shenzhen NTP (China, CVD process). Additional producers include Thomas Swan (UK; CVD process), Nanocyl (Belgium, CVD process), and Bayer (Germany; CVD process). In many instances, these suppliers have established partnerships with device manufacturers to evaluate the suitability of their CNT products for electronic applications. In most cases, the device manufacturers are not producing bulk CNTs, and the CNT manufacturers are not developing devices. An exception here is when CNTs are "grown in place" on device substrates; however, requirements for purification and separation of CNTs tend toward pre-growth, post-processing, and deposition sequences.

The cost of these "new" CNT materials, especially SWCNTs, is still prohibitively high for large-scale applications such as ESD, and current prices reflect research and development costs rather than raw production costs. For example, SWCNTs may achieve electrical percolation in a polymer matrix at a lower wt% than MWCNTs; however, dispersing SWCNTs in polymers is more challenging due to stronger intermolecular forces which cause CNTs to aggregate. Overcoming this challenge will not be commercially

relevant until the cost of SWCNTs drops significantly; the high-quality MWCNTs offered by Showa Denko and others have already fulfilled current market needs.

At the opposite end of the application spectrum where fine control of CNT "order" is required, significant challenges face scalable integration of CNTs. For example, the performance of prospective CNT field-effect transistors is highly sensitive to CNT diameter and metal contact (Figure 6.5). All known SWNT growth techniques produce a population of chiralities (electrical properties), in addition to leaving impurities such as metal catalyst and amorphous carbon in the sample. Therefore, purification and separation (e.g., metallic CNTs for highly conductive films or semiconducting CNTs for transistors) techniques must be advanced.
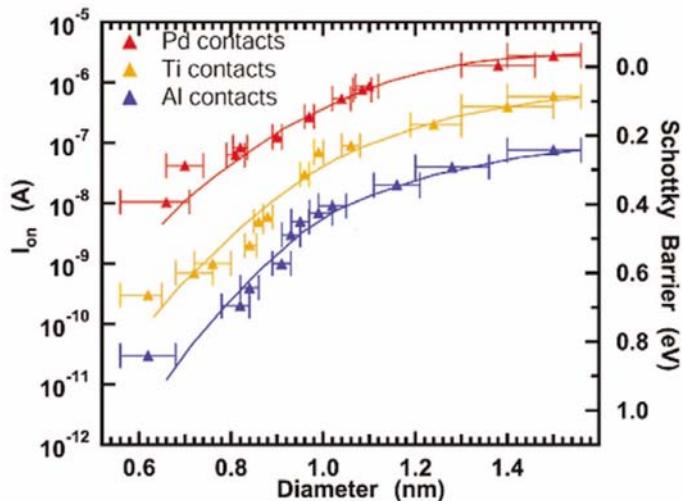
Figure 6.5. Variation of on-current of a CNT-FET as a function of SWNT diameter with three different contact metals (Avouris and Chen 2006).

A new and very promising approach uses density gradient ultracentrifugation to sort CNTs (Arnold et al. 2006). Starting with SWCNTs from the CoMoCat process (Southwest Nanotechnologies), the SWCNTs are dispersed in a solution containing amphiphilic and bile salt surfactants. The surfactants selectively adsorb based on CNT electronic structure and diameter, and therefore, a density difference is created, and this difference is separated into distinct bands by ultracentrifugation. Repetition of the process improves the fidelity of separation. The outstanding result here is that the diameter distribution of a SWNT solution is narrowed to have 97% content in a 0.02 nm diameter range, mostly representing the chirality (0.76 nm diameter) (Ebbesen and Ajayan 1992; Oberlin, Endo, and Koyama 1976). Further understanding of the surfactant-CNT relationship shows promise for tailoring recipes to separate SWCNTs into populations having desired diameter and metallicity, and the process should be scalable to industrial-size centrifuges. Further, once these exquisitely pure materials are available, only very small quantities will be needed to make large numbers of devices, and these could bear high market cost.

LEADING ELECTRONIC AND OPTOELECTRONIC APPLICATIONS OF CNTS

Composites for Electrostatic Discharge and Electromagnetic Shielding

The first commercial applications for MWCNTs make use of their properties to address electrostatic discharge. For ESD applications, the electrical conductivity and high aspect ratio of MWCNTs are exploited to form an electrically percolating nanotube network, at low loading (a few wt%), within an otherwise high electrical resistivity plastic. This prevents static charge build-up on the surface of the plastic and constitutes a core business for Hyperion Catalysis International. Hyperion sells the nanotubes premixed within thermoplastic master batch and ready-to-use formulations. These have found use in the automotive industry in conductive nylon for fuel lines, connectors and fuel filter housings, as well as in exterior plastic parts that must be conductive in order to permit their electrostatic spray painting. Other ESD business opportunities exploited by Hyperion include clean-room components where electrically-charged plastics degrade the environment by collecting dust, and plastic components used in the microelectronics industry (both in chip

fabrication and in component packaging) which is increasingly sensitive to ESD-induced chip failures as insulating layers and channel lengths continue to shrink.

Electromagnetic interference shielding applications differ from ESD principally in that EMI shielding requires a significantly higher conductivity. This can be achieved by increased loading of MWCNTs within the composite matrix; however, at some loading fraction, the mechanical properties of the composite are typically degraded. Another problem associated with high nanotube loading is the very large increase in the viscosity of the melts for thermoplastics or the polymer precursor for thermosetting compounds.

Good dispersion of the nanotubes within the composite body is the key to the highest electrical conductivity, while minimizing degradation (or potentially enhancing) mechanical properties. This relates to one benefit of the less well-graphitized walls of CVD-grown MWCNTs. These are less subject to the van der Waals bonding that makes well-graphitized MWCNTs and the SWCNTs more difficult to break apart for achieving uniform dispersion. The highly defective sidewalls of CVD-grown MWCNTs also provide reactive sites for functionalization with groups meant to further facilitate their dispersion. Possible trade-offs in the electrical conductivity, and/or the mechanical integrity of the composites due directly to the less well-graphitized sidewalls remains an open question at this time.

Potential ESD and EMI applications for MWCNTs remain a common theme in research facilities around the world. For example, Prof. Wei Fei's group at the Department of Chemical Engineering of Tsinghua University has done experiments loading 0.1%–1.6% (mass percent) of their own mass-produced, CVD-grown MWCNT in PET, PET fibers, and PEEK polymers. They claim excellent dispersion and electrical properties, but there is a degradation in tensile strength.

Although the present cost of SWCNTs makes them prohibitive for commercially competitive ESD and EMI applications, they have been explored by researchers in anticipation of eventual price reductions. Measurements indicated a percolation threshold in epoxy of 0.062 wt% SWCNTs, which they ascribe to a very good dispersion of the SWCNTs within the epoxy matrix (Figure 6.6) (Li et al. 2006). At 10–15 wt% loading, Professor Chen reported an attenuation of 20 dB. He also reported high radar shielding (reflectivity) in the S-band. Interestingly, the peak of the S-band reflectivity was observed to shift with the nanotube loading so that with a multilayer design, in which each layer possesses a different loading, they anticipated production of a broad band "absorber" able to cover the S-band.
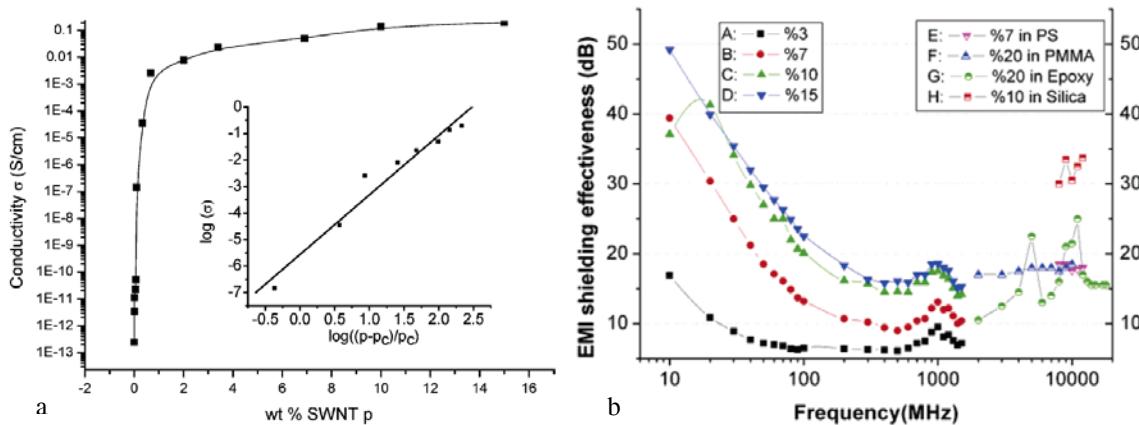
Figure 6.6. (a) Electrical percolation in SWNT-polymer composite, reached at 0.062% of "long" CNTs made by arc discharge using a Ni/Y catalyst; (b) EMI shielding effectiveness of SWNT (curves A-D) and MWCNT (curves E-H) composited (Li et al. 2006).

Batteries and Supercapacitors

Lithium ion batteries appear to be the second major commercial success for MWCNTs. Showa Denko, which supplies its VGCFs for this application (major customer, SONY), announced new production facilities to keep up with anticipated demand, going from a 40 ton/year capacity to 100 tons/year (facilities to come on line in 2007). The main constituent of the anode in such batteries is meso-carbon microbeads that become intercalated with Li ions as the batteries are charged.

Dimensional changes occurring through repeated cycling decrease electrical connectivity between microbeads, degrading performance and limiting cycle life. The addition of ~10% MWCNTs to the anode keeps the microbeads in electrical contact by bridging the nanotubes from bead to bead. In addition to increased cycle life, overall performance is enhanced by improvement of the overall conductivity of the anode. While this represents a significant commercialization success, Li ion batteries constitute a small fraction of the overall battery market.

Work reported to the WTEC team by Prof. Zuolong Yu, CAS Chengdu Institute of Inorganic Chemistry, indicated that nanotubes improved the performance/cycling life for all types of batteries, including lead acid, nickel metal hydride, and Li-ion batteries. This indicates that substantial further battery applications remain to be tapped.

For Li-ion batteries, in addition to a MWCNT anode, Prof. Yu's group has also used MWCNTs coated with $LiCoO_2$ as the cathode. The latter material was also employed in supercapacitor electrodes where a $LiNi_{0.8}Co_{0.2}O_2$/MWCNT composite was shown to have specific capacitance of 285 F/g. In these applications, smaller diameter nanotubes were typically found to have better performance, presumably due to their increased accessible surface area per unit mass. A key finding is that nanotubes mixed with other carbons (e.g. graphite micropowders or acetylene black) show enhanced capacities over either material alone. An important (proprietary) technology Prof. Yu's group has developed for fabricating battery electrodes is the ability to disperse MWCNTs in high concentrations while still retaining reasonably low viscosities.

Supercapacitors, while possessing lower energy storage capacity than batteries, are able to deliver their energy at far greater rates, making them important for numerous applications, for example, in future electric vehicles, where high rates of acceleration are intermittently needed.

Prof. Morinobo Endo of Shinshu University, Japan, described to WTEC panelists the incorporation of chemically modified MWCNTs as an additive material to enhance the electrical conductivity of phenolic-resin-based activated carbon electrode that is most widely used in supercapacitor industries as electrode active material.

Fuel Cell Electrodes and Catalyst Supports

Owing to the electrical conductivity and high specific surface area of CNTs, there is growing exploration of CNTs as permeable electrodes in fuel cells (where the catalyst is in contact with the proton/electron charge transfer media and is electrically connected to the support electrode), and more generally as support materials for nanostructured catalysts. Catalytic metal nanoparticles can be deposited on CNTs by a wide variety of methods such as by electrode position of Pt or Au (Quinn, Dekker, and Lemay 2005), or by solvent-mediated cross-linking. High catalytic activities of catalyst-coated CNTs have been measured and attributed to many effects, including uniform dispersion of metal nanoparticles on CNT surfaces and low charge transfer resistance between the CNT and the electrolyte. However, the mechanism of this favorable interaction is a subject of much ongoing study; for example, there is evidence that surface defects and edges may dominate the catalytic activity of the CNTs (Banks et al. 2005), suggesting that defective CNTs, or stacked graphite "cup" or "cone" nanostructures, may be the most effective catalyst supports (Kim et al. 2004). Another direct advantage of uniform dispersion and high performance of metal-coated CNTs is the potential to reduce the mass of catalyst metal necessary for a particular application (Matsumoto et al. 2004), as some of these metals (e.g., Pt, Au) are very expensive.

Initial work by Wang and colleagues demonstrated platinum-coated MWCNT electrodes in a proton exchange membrane fuel cell (PEMFC) (Wang et al. 2004). The MWCNTs were grown by CVD after electrode position of Co catalyst on carbon paper, giving a surface area of 80–140 m^2/g, compared to 2 m^2/g for the bare paper. Pt catalyst was electrodeposited on the paper after CNT growth. Cyclic voltammetry demonstrated performance of the CNT electrodes far below that of a conventional PEMFC using a carbon black catalyst support; however, high-density, small-diameter CNTs and smaller-diameter Pt catalyst particles were suggested as routes to improve the performance of the CNT-based device.

Further along these lines, NEC Corporation, which the WTEC team visited in Japan, is developing single-wall carbon nanohorns (SWNH). These distant relatives of SWCNTs are single-layered closed shell graphene structures typically 2–3 nm in diameter; however, nanohorns are only several tens of nanometers long and are capped by horn-shaped tips. A main characteristic of the nanohorns is they aggregate in flower-like clusters

("dahlias") typically ~100 nm in diameter, and the spacing between the nanohorns in the aggregates determines their porosity (Bekyarova et al. 2005). Particularly after treatment (e.g., oxidation) to open their tips, or by chemical etching to create defects in their sidewalls, nanohorns provide extremely large surface area and provide a pore structure for gas and liquid to permeate to the inside (Yang et al. 2005). Having extremely low density, SWNHs can be made by CO_2 laser ablation of graphite and already are produced at a level of hundreds of grams/day at the NEC laboratory. Therefore, compared to SWCNTs, nanohorns are expected rapidly to become a low-cost raw material. Deposition of palladium nanoclusters on SWNH aggregates has been achieved by a reduction of $PdCl_4^{2-}$ in the presence of polyvinylpyrrolidone (PVP), which stabilizes the ions into nanoclusters and facilitates attachment to the nanohorns.

During the team's visit, NEC mentioned applications electrochemical storage devices (batteries) and fuel cells using nanohorns (electrodes). Light weight and high electrical conductivity and thermal stability make nanohorns a useful material in energy storage. NEC has produced press releases discussing batteries and fuel cells using nanohorns, but it is unclear as to whether NEC intends to pursue this as a major thrust. According to NEC, nanohorn cell phone batteries are now being developed, and Nissan Motors has invested large capital to develop fuel cells from them.

Another significant effort is the collaboration between Carbon Nanotechnologies, Inc., Motorola, and Johnson Matthey, Inc., which, in 2004, received a $3.6 million NIST grant to develop free-standing CNT electrodes for fuel cells. This effort is targeted for fuel cells to replace rechargeable batteries in portable electronic devices such as mobile phones and laptop computers. However, no further updates were found on this project.
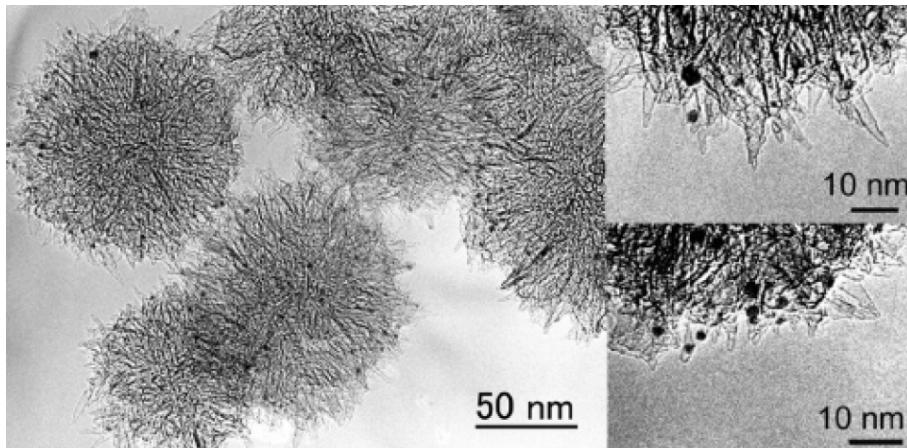
Figure 6.7. Aggregates of single-wall carbon nanohorns coated with ~2 nm diameter Pd nanoclusters attached using poly(vinylpyrrolidone) (Bekyarova et al. 2005).

Emission Sources: Displays and X-Ray Emitters

Samsung Display Innovation (SDI), a division of Samsung Corporation, is developing a field emission display using CNTs as the field emission source. The study panel visited SDI's facility outside Seoul, Korea, and was hosted by Dr. Young Chul Choi. SDI has been developing the FED for six years after receiving initial funding from the Korean government; Dr. Choi currently has 70-80 employees dedicated to the project.

The Samsung CNT FED is microfabricated on display glass and features a triode structure, where a bias voltage is applied between the bottom (cathode, ITO) and middle (gate) electrodes, and the emission is focused by the top electrode (Choi et al. 2006) (Figure 6.7). Each pixel contains many CNT emitters. The CNT emitters are applied to the device by screen-printing of a custom-made CNT paste, or by direct growth of CNTs by CVD. In the former case, commercially available CNTs are mixed with many ingredients, and the paste is wiped through a screen mask that is placed over the device (Choi et al. 2004). In the latter case, a catalyst layer is deposited (e.g., sputtered invar) on the device, and the CNTs are subsequently grown by thermal CVD of CO/H_2. For screen printing of the paste, the maximum (and therefore limiting) process temperature is that of firing the paste after printing (<450°C); for CNT growth, the CVD temperature is limiting (lowest 420°C so far; must be <500°C to prevent melting of the glass). While isolated vertically

aligned CNTs as grown by the CVD process are generally desired for field emission, the CNTs in the paste are generally tangled and parallel to the substrate. Therefore, CNTs as-deposited by the paste method are tipped upward by applying and peeling a tape from the CNT substrate surface.

Owing to its versatility and scalability to large substrate areas, the paste method is preferred and is being pursued for current prototype development. Many types of CNTs (e.g., SWCNTs, MWCNTs, DWCNTs with various diameters and lengths), obtained from many suppliers, have been evaluated by this method. It is believed that SWCNTs generally exhibit a higher field emission density, yet lower lifetime, while MWCNTs exhibit lower emission density, yet longer lifetime. Therefore, a careful tradeoff must be made to optimize device performance. Currently, uniform-length, high-quality, small-diameter MWCNTs are preferred (MWCNTs are also easier to disperse than SWCNTs); a price of approximately US$10/gram would be suitable for commercial production of the CNT FED.

So far, SDI has made prototype CNT FED displays in the 5–15" range. The CVD growth process limits the size of SDI's CVD chamber (currently 1 m diagonal); however, up to 70" displays can be made by the paste method. The initial target market is 30–50" displays, while smaller displays will be of OLED and LCD types, and larger displays will be plasma type. SDI also anticipates continued development for one year and having a product on the market in two to three years.

The development team identified many achievements and remaining challenges in the FED program. A main challenge related to use of CNTs in the display is the uniformity of emission. This is improved by adding a resistive layer under the CNT paste and may be further managed by independently adjusting (calibrating) the voltages over the array to give uniform emission. A lifetime of 30,000 hours is sought, and the SDI team believes this can be achieved by its technology. Also, as the display size increases, maintaining good vacuum sealing is an increasing challenge, and inadequate vacuum decreases the lifetime as the emitters decay more quickly.

The application of CNTs as x-ray emission sources has been led by Otto Zhou's group at the University of North Carolina, and is being commercialized by Xintex, Inc. (co-founded by Prof. Zhou, www.xintek.com/index.htm). In a CNT-based x-ray source (Figure 6.8), CNTs are placed in a triode configuration as a field electron emitter; the emitted electrons are incident upon a target (typically Mo) which, in turn, emits x-rays and is aimed toward the sample (Cheng et al. 2004). Overall, imaging systems using CNT x-ray emitters offer promise over current technology due to their small size, fast response time, and capability for multiplexing and array imaging. These seek to enable rapid, high-resolution imaging without the need for moving the source and/or detector as is typical in many current x-ray and CT imaging systems. Similar to field emission displays, CNT x-ray emitters can be arrayed as "pixels," and imaging is facilitated by the rapid response time of the emitters along with frequency division multiplexing using a single flat detector (Zhang et al. 2006). CNTs can be integrated in x-ray emitters by direct growth on the emitter substrate, or by post-growth deposition, and therefore, face similar manufacturing challenges as field emission displays. However, displays require further integration with circuit architectures and immediately need finer pixel resolution. In a prototype device, purified SWCNTs were electrophoretically deposited in a tangled morphology on a metal substrate, which was then incorporated in a sealed emitter tube (Figure 6.9) (Zhang et al. 2005). Prof. Zhou (2006) explained that a CNT emitter tube is stable for over 100 hours of operation (36 million cycles), with a constant voltage pulse 10 μs width at 100 Hz. The emitter current exceeds 1 A.

There is much other work in emitter applications of CNTs; however, the Samsung display is by far the most serious commercial effort. During the team's visit, Iljin Nanotech (Seoul, Korea) mentioned development efforts using CNTs for field emission light sources and reports international patent filings on the topic. The group of Prof. Shoushan Fan at Tsinghua University (Tsinghua-Foxconn Nanotechnology Research Center, Beijing, China) is testing prototype field emission lamps using CNT-coated wires sealed inside phosphor-lined tubes. These are sought as ambient light sources to replace fluorescent tubes; however, the power consumption must be reduced significantly for practical application. Field emission from the ends of CNT yarns is also being studied (Wei et al. 2006). Thermionic CNT yarn emitters are sought as a long-life replacement to LaB_6 filaments that are commonly used in electron microscopes (Liu et al. 2006). In general, CNTs are sought for field emission because of the high current density due to their high aspect ratio; however, many other nanomaterials (e.g., small-diameter nanowires, diamond nanocrystals, nanofabricated

metal tips) exhibit structure-based and surface-based field emission and will be part of competing technologies.
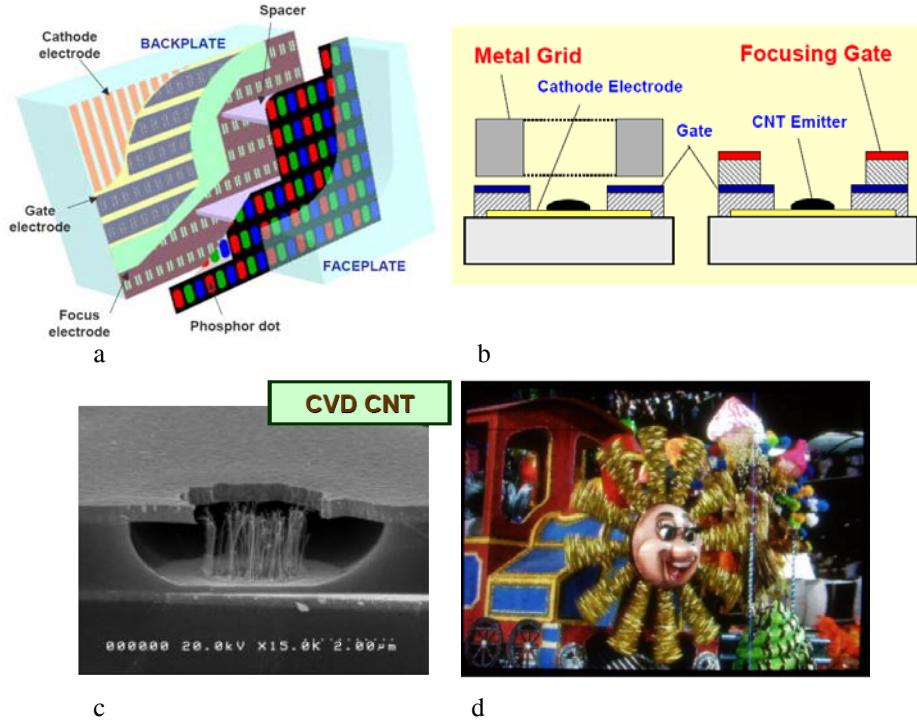
Figure 6.8. CNT field emission display (a,b) schematics of display structure and triode pixel architecture; (c,d) SEM image of individual pixel with aligned CNTs grown directly on substrate, and image of prototype 15" diagonal display (Courtesy of Samsung SDI).
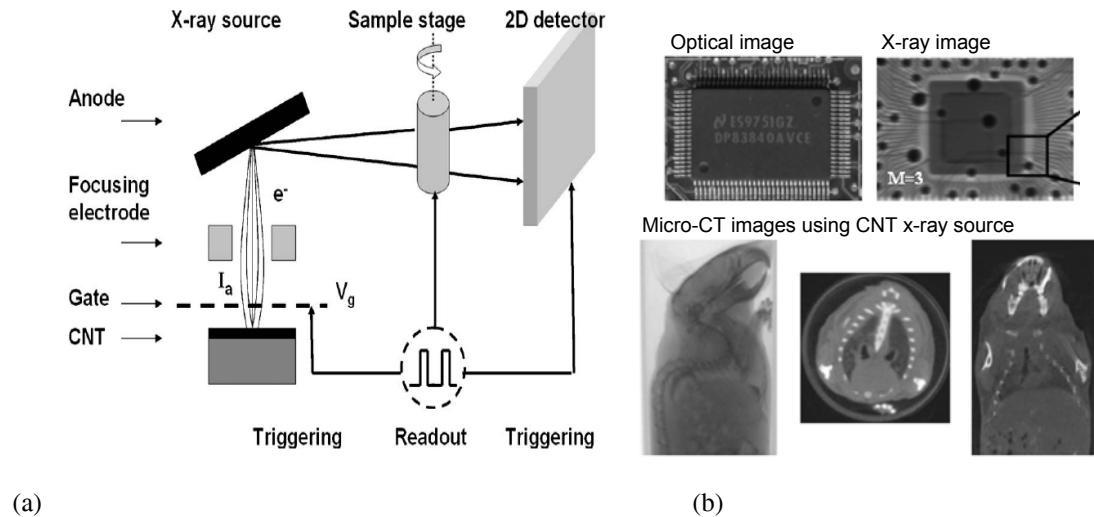
Figure 6.9. (a) Schematic of CNT x-ray emission source (Zhang et al. 2005); (b) x-ray and computed tomography images of a computer chip and a mouse carcass, obtained using CNT-based x-ray source.

Transparent Conductors

Work at the University of Florida, led by Prof. Andrew Rinzler, is developing CNT films as conductive transparent electrodes for applications that include organic light-emitting diodes, organic solar cells, and supercapacitors. Typically, the films are prepared from purified SWCNTs grown by laser ablation. The CNTs are dispersed in an aqueous surfactant and deposited on a porous polymer membrane by vacuum filtration. The CNT-coated membrane is then adhered to the desired substrate, and the polymer is dissolved in a solvent bath, leaving the CNT film on the substrate. The resulting CNT film is optically transparent and electrically conductive, having conductivity exceeding the best conducting polymers, and > 80% transmittance from visible to mid-IR wavelengths (Wu et al. 2004).

One of the features claimed for these transparent films is the high surface area of the nanotubes for coupling electronically to the active organic medium. Rinzler's group has found, however, that the nanoscale porosity in the films is less than optimum for infiltration with the active polymers. While on the CNM study tour in China, Rinzler described a method to introduce far greater controlled porosity into the films. This consists of co-depositing sacrificial nanoparticles along with the nanotubes to form composite films from which the nanoparticles are subsequently dissolved, leaving size-controlled nanoscale pores throughout the body of the films. The standard films were described as exhibiting a density of 0.77 g/cm^3; porous films of the same area and mass of SWCNTs have an eight-fold reduction in density (~0.1 g/cm^3). The increased porosity was evidenced by SEM and atomic force microscope (AFM) imaging, and by a comparison of the electrolytic capacitance between a standard and porous films (40% increased capacitance in the latter). Optical imaging showed that the increased porosity introduced only a slight haze in the films, while electrical measurements showed the sheet resistance was also only slightly degraded, going from 75 Ω/square to 100 Ω/square.

Eikos Corporation is also developing CNT films as transparent conductors, particularly for displays; the films can be deposited by roll-to-roll and conventional printing techniques (www.eikos.com/advantages. html).

Electromechanical Devices: Memory, Relay, and Others

Owing to their mechanical resilience (e.g., reversible bending and high-cycle fatigue) and electrical conductivity, CNTs are also sought for nanoelectromechanical devices such as nonvolatile memory and relays. Most notably, Nantero is developing a CMOS-integrable memory device ("NRAM") using thin films of SWCNTs. This concept was conceived and demonstrated as a "crossbar" architecture where each bit is a cross-junction between isolated SWCNTs. This bistable configuration can be actuated electrostatically and interrogated by reading the electrical resistance of the junction (Rueckes et al. 2000). (Because it is, so far, impossible to fabricate a large crossbar array by either direct growth — which would also necessitate CMOS-compatible temperatures — commercialization of this idea realized the device using a suspended-ribbon architecture as shown in Figure 6.10, where a membrane 1–2 nm thick of CNTs is electrostatically deflected to contact a bottom electrode where it reversibly adheres to the electrode due to van der Waals interactions.) Rob Smith of Nantero reported that current devices have been switched over 50 million cycles, at operating voltages below 5 V, with switching times below 3 ns (Smith, 2006).

A further important commercial aspect of Nantero's effort is the integration of CNTs into a CMOS process, where presumably SWCNTs are purified and dispersed in a solvent, and then the solvent is coated onto wafer substrates and can be subsequently patterned and etched using lithographic techniques. This could enable CMOS-compatible fabrication of other devices, including digital logic, reconfigurable antennas, sensors, and RF devices, without necessitating CNT growth on these devices.

There are many other electromechanical devices using CNTs; however, these are largely at the single-device research stage. For example, telescoping "sword-in-sheath" extension of a MWCNT provides a demonstration for a nanoscale linear bearing, having no measurable wear between the sliding wall surfaces (Cumings and Zettl 2000). Extending this idea, a telescoping MWCNT is built as a tunable electromechanical resonator, having $\approx$200 MHz oscillation frequency (Jensen et al. 2006). A single suspended SWNT has been implemented as the transducer element in a microfabricated pressure sensor, where deflection of a suspended Al_2O_3 membrane strains the SWNT and thereby changes its current-voltage (I-V) characteristics (Stampfer et al. 2006). Prof. Yungwoo Park, whom the team met while visiting the NANO Systems Institute (NSI, nsi.snu.ac.kr) at Seoul National University (SNU), is developing a three-terminal CNT relay in collaboration with Chalmers University in Goteborg, Sweden (Lee et al. 2004). This features a single cantilevered (overhanging) CNT that is electrostatically actuated to contact patterned electrodes on the substrate.

Concept (1998)
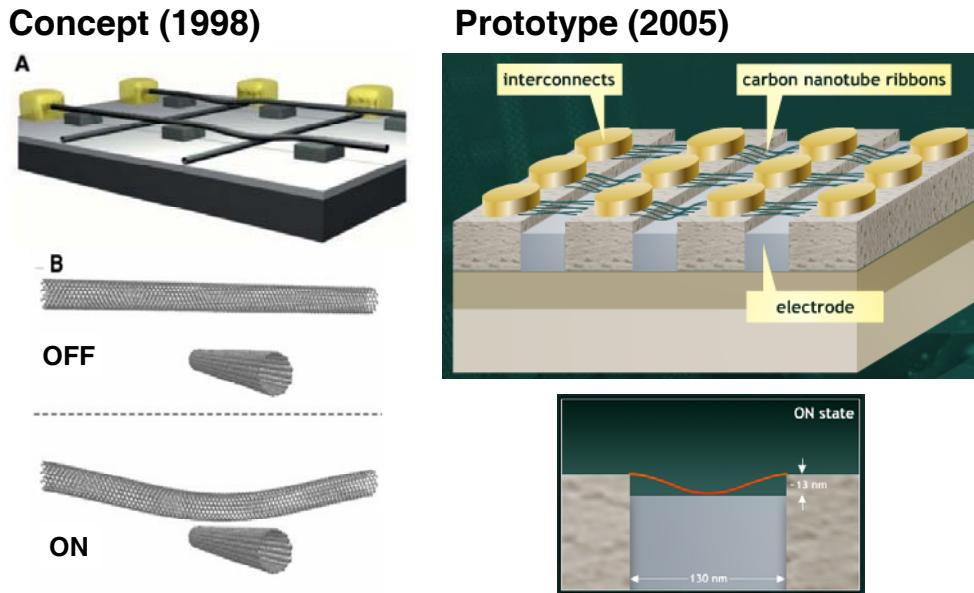
Prototype (2005)

Figure 6.10. Concept (Rueckes et al. 2000) and prototype schematic of nonvolatile CNT memory device using bistable electromechanical junctions of suspended CNTs.

Microelectronic Interconnects

Fujitsu is developing CNTs as microelectronic interconnects, primarily as vertical via structures for integration in microelectronic devices. Compared to present-day copper interconnects, individual CNTs offer potential for higher current-carrying capacity (1000 times that of copper, according to Fujitsu), thermal conductivity (10 times that of Cu) and mechanical strength. As microelectronics progresses to finer resolution, smaller-diameter interconnects are required, and therefore, these interconnects must handle a higher current density. Fujitsu projects that CNTs are necessary for 32 nm line width processing and beyond, where the required current density will exceed 10^6 A/cm^2; this crossover is expected between years 2010 and 2015.

Fabrication of CNT interconnects poses significant challenges, including low-temperature (< 500°C) growth for compatibility with back-end CMOS processing, high-density growth of high-quality CNTs to achieve high electrical conductivity in via bundles, growth on full wafer areas, and growth on electrically conducting underlayers. Fujitsu has made significant progress in all these areas and has widely published its progress as the critical performance characteristics (e.g., via conductivity and current-carrying capacity) have improved (Nihei, Kawabata. and Awano 2005; Horibe et al. 2005). Using a multimode (RF plasma, DC plasma, hot-filament, and thermal) CVD chamber, Fujitsu researchers have studied growth of MWCNTs and have scaled the process to obtain uniform growth on full 300 mm wafers. Fujitsu has studied many catalyst combinations and underlayers; for example, a Co catalyst film deposited on a tantalum/titanium (Ti/Ta) barrier layer seeds vertically aligned MWCNTs while maintaining electrical contact to a Cu layer beneath the Ta (Figure 6.11). Then, the vias are capped with Ti and Cu layers for top-layer electrical contact. More recent work has been with gas-phase-deposited Ni and Co nanoparticles as catalysts (Sato et al. 2005; Sato et al. 2003); this has grown 4 nm diameter CNTs at a local density of 9×10^{11}/cm^2 at the bottoms of via holes as small as 40 nm in diameter. Individual vias have been operated with no degradation for over 120 hours at an equivalent current density of 2×10^8 A/cm^2 in each CNT. Via growth from Co nanoparticles on TiN/Ta/Cu has achieved a per-via resistance of approximately 0.5 Ω; however, this still far exceeds resistance of a Cu via, which is typically 0.01-0.1 Ω (Figure 6.11).
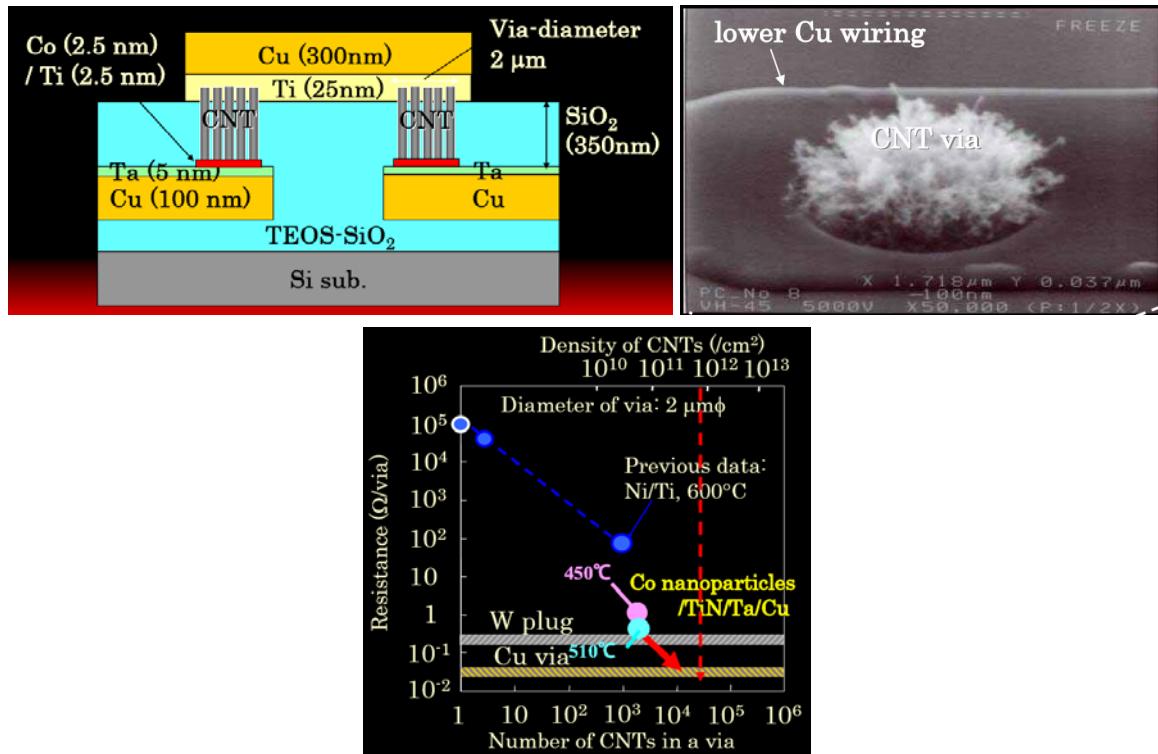
Figure 6.11. Integration and performance of vertical CNTs as microelectronic interconnects.

Chemical Sensors

The high electrical conductivity and surface area of CNTs is motivating their application as chemical sensors for detection of trace contaminant and hazardous vapors for industrial process control, security applications, and for breath analysis in medical diagnostics (Snow, Perkins, and Robinson 2006). This is particularly true for SWCNTs, which have the highest specific surface area and, therefore, are most sensitive to the presence of nearby molecular species and molecular adsorbates. Typically, a CNT-based chemical sensor consists of a tangled network (film) of CNTs that are electrically connected to a substrate (Figure 6.12.) in a resistive sensor; the CNTs are connected between electrode pairs such as interdigitated fingers, and in a capacitive sensor, the capacitance between the network and the substrate (isolated by a dielectric layer) is also monitored. Chemical adsorption on a CNT surface is driven by the partial pressure of the analyte relative to its vapor pressure (rather than relative to the ambient pressure); therefore, CNT sensors can detect low concentrations of low vapor-pressure analytes such as explosives where many conventional sensors are unable to do so.
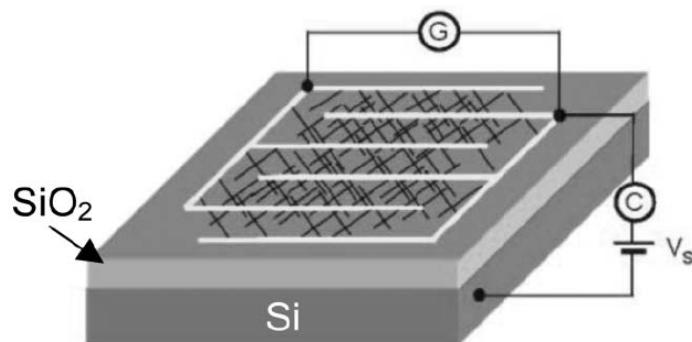
Figure 6.12. Typical architecture of a chemical sensor using a CNT network, where tangled CNTs are in contact with interdigitated electrodes, and the conductance and capacitance of the network is measured using external circuitry (Snow Perkins, and Robinson 2006).

Initial work by Kong and colleagues in 2000 demonstrated that adsorption of a molecule on the surface of a SWNT causes a transfer of charge (i.e., donation or withdrawal of an electron) to the SWNT, and therefore, changes its electrical conductivity (Kong et al. 2000). Many adsorbates bind strongly to CNTs. Here, the sensor must typically be heated or exposed to ultraviolet light to remove the adsorbate from the CNT surfaces and therefore "zero" the signal. Further, the sensitivity of a CNT to charge transfer interactions (i.e., how many electrons are transferred/withdrawn per adsorbed molecule) depends on the electronic structure (i.e., chirality) of the CNT and adsorbed molecule. A general strategy to increase sensitivity (i.e., minimum detectable concentration) and/or specificity (i.e., response to a particular desired species) is to coat the CNTs with a polymer that selectively adsorbs a particular molecule or class of molecules. For example, coating a SWNT network sensor with polyethyleneime (PEI) allows detection of 100 ppt of NO_2 in a response time of 1000 seconds(Pengfei, Vermesh. and Grecu 2003). As an aside, while the sensitivity of electrical conductivity to surface adsorbates can be helpful for CNTs as chemical sensors, it is important to consider these "environmental" effects in the context of stable operation of CNTs as other device elements such as transistors (Collins et al. 2000).

The resistivity of a SWNT can also change due to collisions with gas molecules. This has been demonstrated by measuring a resistance increase across CNT network devices upon exposure to inert gases (Romero et al. 2005). This change is proportional to the molecular mass of the gas (as $M^{1/3}$), so a heavier molecule makes a larger "dent" in the sidewall of the CNTs. The authors hypothesize that the collisions introduce a new channel, which scatters conduction electrons traveling through the CNTs. Since this phenomenon depends on the ambient composition and temperature, it may require consideration for high-precision gas sensing using CNTs.

Adsorbed gases can also be sensed by measuring the capacitance of a CNT network; compared to resistive sensing, this method is faster and more responsive to a wider variety of vapors. When an electric field is applied between a CNT network and the underlying "gate" electrode, molecules adsorbed on the CNT surface are polarized, and this increases the capacitance between the network and the gate (Snow et al. 2005). With a minimum (reversible) detectable capacitance change $\Delta C/C = 10^{-4}$, part-per-billion detection limits for nerve agent and explosive vapors are expected (Snow Perkins, and Robinson 2006). Simultaneous resistive and capacitive sensing can further identify vapors based on their relative responses (Snow and Perkins 2005), and detection algorithms, such as those using artificial neural networks, are sought to identify analytes from the outputs of sensor arrays (Shi et al. 2006). For CNT sensors, resistive sensing is preferred for analytes that give a large charge transfer; capacitive sensing is better for analytes that transfer less charge as it offers increased sensitivity, larger dynamic range, and faster response (Snow Perkins, and Robinson 2006).

For commercial viability, CNT sensor systems must reliably detect and identify target vapors in ambient atmospheres containing many other species and under varying temperature and humidity. Therefore, further development of sensor arrays along with chemical-specific coatings, preconcentration techniques, and signal analysis algorithms is necessary. Commercial efforts in nanomaterial- and CNT-based chemical sensors are known to be under way by many small startup companies, although details of particular efforts are not readily available and should not be speculated upon. The broad potential merits of CNT sensing appear to be in portability, sensitivity for pre-identified targets, and small size. More complex techniques, such as mass spectrometry and ion mobility spectrometry, will likely maintain superiority for chemical analysis and nonspecific agent detection.

Micro-/Nanoelectronic Device Elements: Transistors, Oscillators, Diodes

The development of single CNT field effect transistors (CNTFET) as successors for Si-based devices in recent years has been led by P. Avoris and the IBM group, and by Prof. Hongjie Dai's group at Stanford University. Many promising results have been demonstrated in the course of optimizing individual transistors. Mobility as high as 100,000 cm^2/Vs has been reported with micrometer long channel CNTFETs (Durkop, Getty, and Cobas 2004); quasi-ballistic transport was reported for short channel (< 100 nm) devices (Javey, Guo, and Paulsson 2004). Due to the lack of surface dangling bonds, high κ dielectic materials can be directly incorporated to achieve better performance (Javey et al. 2002). Because a Schottky barrier (SB) forms between the interface of metal contact and the CNT, the transport behavior and scaling principles differ from the conventional Si metal-oxide-semiconductor field-effect transistors (MOSFETs) (Heinze et al. 2003). A double gate CNTFET structure has been designed to allow separate control of the switching of the SBs and the CNT channel, and faster switching of the transistors was demonstrated with a subthreshold

swing value lower than the thermal limit. Dopings of the CNTs have enabled both p- and n- type transistors and CNTFET complimentary logics (Javey et al. 2005).

The step following the optimization of the individual transistors is to integrate the CNTFETs into logic circuits. At the WTEC North American workshop, Dr. Jia Chen from IBM reported the fabrication of a five-stage ring-oscillator (RO) on a single 18 μm long CNT (Chen et al. 2006). ROs are essential for the characterization of the ac properties of CNTFETs. Five pairs of p- and n-type CNTFETs in CMOS configurations are wired along an ambipolar CNT, and two different metals are used to construct the top gates: Pd for the p-type and Al for the n-type transistors. The work function difference of the two metals effectively shifts the FET thresholds, and p- and n- behavior are thus implemented. The complete circuit is shown in Figure 6.13(a). With this circuit, an oscillation frequency of up to ~70 MHz has been achieved (at VDD = 1 V), which corresponds to a delay of 1.4 ns per stage (Figure 6.13(b)). This frequency is much higher (~105 times) than those achieved by oscillators based on different CNTs (Javey et al. 2002; Bachtold et al. 2001). More importantly, it does not represent an inherent limitation of the CNTs, which is expected to be in the terahertz range (Burke 2004). Further improvement in fabrication can eliminate the parasitics of the circuit, and better performance is anticipated.
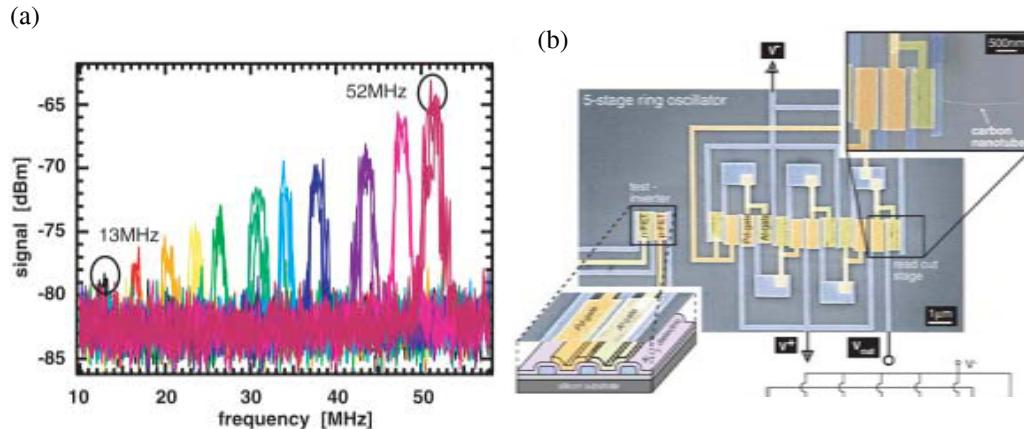
Figure 6.13. (a) Scanning electron microscope image of a five-stage CNT ring oscillator circuit; (b) voltage-dependent frequency spectra (Chen et al. 2006).

Also at the WTEC North American workshop, Dr. Ji Ung Lee from GE Global Research Center reported the fabricaton of *p-n* junction diodes with close to ideal rectification characteristics. The diode devices were built by using a pair of split gate electrodes under single CNTs (Figure 6.14a). Photovoltaic effects were demonstrated with these devices, and significant power conversion efficiencies were obtained owing to enhanced properties of these almost ideal diode devices.
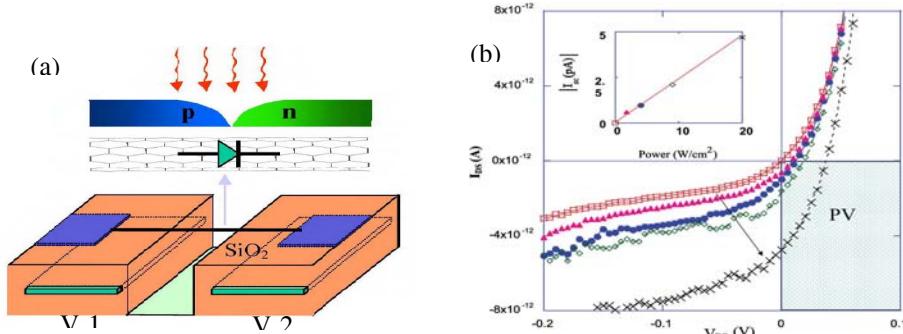
Figure 6.14. (a) The split gate device where Vg1 and Vg2 are biased with opposite polarities ($V_g1 = -V_g2 = +10V$) to form an ideal *p-n* junction diode along an SWNT; (b) *I-V* characteristics under increased light intensity showing a progressive shift into the fourth quadrant (PV) where the diode generates power. The inset shows the expected linear increase in the current measured at $V_{DS}=0$ (*I*sc) with illuminated power (Lee 2005).

The opposite effect of the above, electroluminescence, i.e., upon the application of a bias, electrons and holes recombine to give out light, was also investigated. It was found that a p-n junction in the CNT is not necessary if the device is ambipolar, i.e., both electron and hole current flow in the CNT electroluminescence can be observed. The recombination site of the electron and hole can move physically along a CNT under the gate voltage, as shown in Figure 6.15(a), since the relative contributions of electrons and holes to the total current is strongly gate dependent (Freitag et al. 2004). The radiation has a characteristic energy that depends on the diameter and chirality of the excited CNT. In addition to the translatable emission, localized electroluminescence is also observed from particular spots on a CNT under unipolar transport conditions (Freitag et al. 2004; Freitag et al. 2006), as long as e-h pairs (excitons) can be actively generated by those spots. This process occurs near defects, trapped charges in the insulator, or any other inhomogeneities that produce voltage drops along the CNT and generate large, local electric fields. Artificial structures can also be fabricated that create the conditions locally, i.e., sudden change in the potential, that generate e-h pairs and light emission (Chen et al. 2005). Such a device is shown in Figure 6.15(b). Thus, a CNTFET device can be used as a transistor, light emitter, or light detector. Choosing among these different modes of operation only requires the bias conditions to be changed.
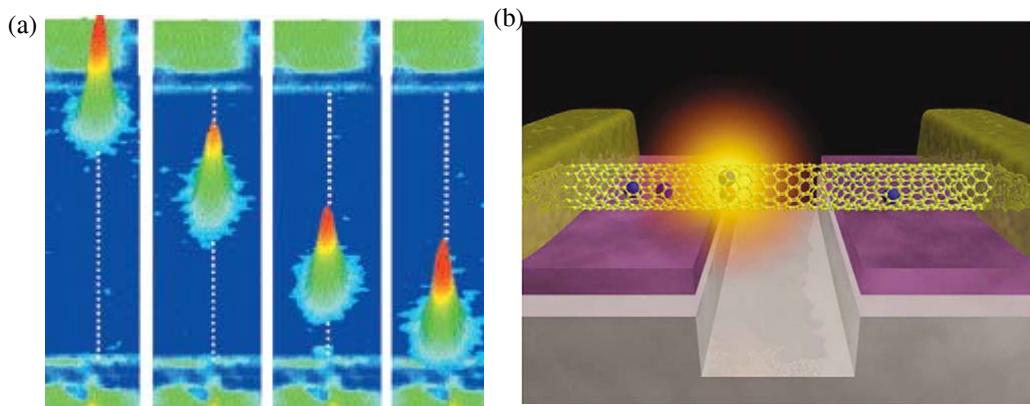
Figure 6.15. (a) Light emission can be translated between the two metal electrodes by varying the gate voltage (Freitag et al. 2004); (b) schematic structure used to generate localized light emission (Chen et al. 2005).

CONCLUSION

This chapter overviewed the electronics-related applications of CNTs that appear to have significant practical potential, and which are generating significant commercial interest. Many other applications that are more at the research stage were not included here.

The promise for applications of CNTs in electronics is widespread. In offering a "menu" of possible electrical characteristics based on their diameter and chirality, along with high mechanical and thermal stability, CNTs could truly enable new and higher-performance electronics ranging from broadband transparent conductors to high-performance transistors and oscillators. However, it is perhaps not widely recognized that MWCNTs have already achieved success in some "bulk" electronic applications, including conductive plastics for electrostatic discharge and rechargeable batteries. These efforts started in the 1980s, well before focused research on SWCNTs ignited in the early 1990s, and have established a broad commercial market for high-quality MWCNTs, which is fulfilled by a manufacturing capacity of over 100 ton/year.

There is currently a significant divide between this established market for MWCNTs in bulk electronics and the emerging market for small-diameter MWCNTs and SWCNTs, where the price of SWCNTs is very high and is driven by research and development costs. Although the electronic applications where SWCNTs are advantageous or necessary will use relatively small quantities of CNTs (a gram goes a long way), many applications seeking these "new" CNT materials will impose significant additional manufacturing requirements, including very high purities and narrow diameter and chirality distributions. Rapid progress is being made in these post-processing areas in addition to CNT synthesis; therefore, technologies that use CNTs after post-growth processing will emerge first. On the other hand, electronic technologies and devices

overall that require individual CNTs "grown in place" will likely be farther behind, as it will take longer to develop a direct growth process that meets these needs. Progress in SWNT separation, such as recently achieved using ultracentrifugation, will make higher-fidelity materials available for characterization and device prototyping, which will also advance our understanding of the application-relevant electrical characteristics of CNTs.

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APPENDIX A. PANELIST BIOGRAPHIES

Peter C. Eklund
Panel Chair

Professor Peter Eklund received his A.B. in Physics from the University of California at Berkeley and his Ph.D. in Solid State Physics from Purdue University. In 1977 Prof. Eklund joined the University of Kentucky (Lexington) as an Assistant Professor in the Department of Physics; he became a full professor in 1986. He was awarded the prestigious University of Kentucky Research Professorship in 1998 for his contributions to graduate education and research discoveries in carbon materials. In 1999 he left the University of Kentucky to join Penn State University where he is currently a professor in the Department of Physics and Material Science and Engineering.

In addition, Professor Eklund has devoted considerable effort to entrepreneurial activities. He has founded four small companies over the past 15 years that survive today. He is currently President/CEO of CarboLex, Inc., a company devoted to the production and sale of large quantities of carbon nanotubes. He founded this company in 1997 with Robert Haddon while they were professors at the University of Kentucky. CarboLex was incubated in the University of Kentucky ASTeCC facility, a technology transfer/commercialization center. Two years prior to initializing CarboLex, with Japanese venture capital, he co-founded the International Center for Materials Research, Inc. (ICMR). ICMR was built around Eklund's work to mass-produce nanopowders produced by CO_2 laser pyrolysis. ICMR moved to Silicon Valley two years later and became Nanogram, Inc. Professor Eklund is a founding member of Nanogram, still a growing company. He also co-founded PhotoStealth, Inc., which first developed a computer-based camouflage design and screen printing technology for hunters and the military.

Professor Eklund's research is driven by his desire to synthesize new materials of fundamental and practical importance with the goal of understanding their physical properties via atomic scale modeling. His research group has been involved in crystal growth, thin film deposition (physical vapor deposition, sputtering, and CVD), intercalation (vapor, electrochemical), and the production of nanoparticles, semiconducting nanowires, and carbon nanotubes. His expertise includes structural characterization (SEM, HRTEM, x-ray and neutron diffraction), electrical transport (resistivity, thermoelectric power), optical spectroscopy (Raman and IR mode spectroscopy, photoluminescence, photoconductivity, reflectivity-optical dielectric function, and ellipsometry). He is widely known for his work in carbon-based materials (including diamond films, graphite and graphite intercalation compounds, fullerenes, nanotubes, and atomically thin graphene films). He has published over 350 research papers in refereed journals, two research monographs, and over 20 review articles and book chapters. He has eight U.S. patents issued and six pending. Recently, his research has focused on hydrogen storage materials, fundamental physics of semiconducting nanowires, carbon nanotubes, graphene, and sensor devices from these filaments.

Pulickel M. Ajayan

Professor Ajayan received his Ph.D. in materials science and engineering from Northwestern University in 1989. After three years of post-doctoral experience at NEC Corporation in Japan, he spent two years as a research scientist at the CNRS Laboratoire de Physique des Solides in Orsay, France, and about a year and a half as an Alexander von Humboldt fellow at the Max-Planck-Institut für Metallforschung, in Stuttgart, Germany.

Professor Ajayan's research interests are mainly focused on the synthesis of nanostructures and the study of their structure and properties in relation to size and confinement. He is one of the pioneers in the field of carbon nanotubes and has demonstrated several possibilities for using these quasi-one-dimensional structures as templates and molds for fabricating nanowires, composites, and novel ceramic fibers.

Major goals of his research include producing macro-assemblies made of nanostructures for applications, understanding growth mechanisms of nanostructures, and designing new structures and multifunctional nanocomposites. Other research interests are phase stability in metal clusters, the graphite-diamond phase transition, and growth of nanostructures under electron irradiation. He has expertise in several different electron microscopy techniques.

Robert Blackmon

Robert Blackmon received his B.S. in Chemical Engineering from Northwestern University in 1994. After graduation, he began working as a project engineer for HPD Products, where he worked for over ten years. HPD Products is a group based in Chicago, Illinois, that specializes in industrial crystallization and evaporation. Blackmon's career at HPD spanned all facets of project development including service and process optimization, project management, process design, and sales. He has worked with clients in a wide variety of roles and geographies and has helped to develop ventures in over 50 countries throughout the Americas, Europe, and Asia.

Currently, Blackmon is the manager of business development at Harper International. Harper International focuses on custom thermal processes in controlled atmospheres. Harper supplies industrial-scale systems for processing of carbon materials at high temperature. At Harper, Robert's main area of interest is expanding market presence into emerging fields, such as nanomaterials.

John Hart

John Hart is a post-doctoral associate at the Massachusetts Institute of Technology, working in the Departments of Mechanical Engineering, Aeronautics and Astronautics, and Materials Science and Engineering. John holds Ph.D. (2006) and S.M. (2002) degrees from MIT, and a B.S.E (2000) degree from the University of Michigan, all in Mechanical Engineering. John received the 2006 MIT Senturia Prize for best doctoral thesis in micro/nano technology, and graduate fellowships from the Fannie and John Hertz Foundation, National Science Foundation, and MIT Martin Foundation. John's research currently focuses on synthesis and applications of nanostructured materials, including carbon nanotubes, microsystems and machine design, and scientific visualizations. In fall 2007, John will become Assistant Professor of Mechanical Engineering at the University of Michigan.

Jing Kong

Jing Kong is a principal investigator in the Research Laboratory of Electronics (RLE) at the Massachusetts Institute of Technology (MIT). She received a B.S. in chemistry from Peking University in 1997 and a Ph.D. in chemistry from Stanford University in 2002. From 2002 to 2003, she was a research scientist at NASA Ames Research Center, and from 2003 to 2004, she was a postdoctoral researcher at Delft University. She joined the MIT faculty in 2004 in the Department of Electrical Engineering and Computer Science. Professor Kong's research interests focus on the problem of combining the synthesis and fabrication of individual carbon nanotubes and integrating them into electrical circuits. Applications of her research include the use of carbon nanotubes as extremely sensitive chemical sensors to detect toxic gases.

Professor Kong is member of the American Chemical Society, the American Physical Society, and the Materials Research Society. She received the 2001 Foresight Distinguished Student Award in Nanotechnology in 2001, the Stanford Annual Reviews Prize in Physical Chemistry in 2002, and the MIT 3M Award in 2005.

Bhabendra Pradhan

Bhabendra Pradhan received his Ph.D. in carbon science from the Indian Institute of Technology at Delhi in 1997. Dr. Pradhan joined the Institute for Chemical Reaction Science (ICRS) at Tohoku University in Japan in 1997 as a researcher, where he worked on template techniques to synthesize carbon nanotubes and the introduction of transition and noble metal into the channel of carbon nanotubes. In 1999, he joined as senior research associate at Penn State University in the Energy Institute and later in the Department of Physics, where he worked on synthesis, purification, and use of carbon nanotubes for hydrogen storage. Dr. Pradhan is the author of more than 90 scientific publications. He also has four patents issued in the United States and Japan, and ten additional patent applications. He currently holds the position of Principal Scientist/and Group Leader of Nanomaterials R&D at Columbian Chemicals Company.

Dr. Pradhan's research interests include the synthesis and microstructure of nanomaterials, e.g., carbon nanomaterials, nanowires, and nanoceramics. He is also devoted to study of the surface chemistry of carbon nanomaterials (purification and functionalization of carbon nanomaterials, catalysis, and adsorption) and energy storage in carbon nanomaterials (hydrogen storage, Li-ion battery, and supercapacitor, noble metal-supported catalysts.)

Apparao Rao

Apparao Rao received a B.S. in physics (1983) from Bombay University, India. His Ph.D. is in condensed matter physics (1989), from the University of Kentucky. Professor Rao's laboratory at Clemson University focuses its research primarily on the synthesis and characterization of carbon nanotubes. He is dedicated to understanding the properties and applications of single-wall and multi-wall carbon nanotubes.

Other research topics of Professor Rao include characterization of semiconducting nanobelts, nanowires, and thermoelectric materials. As tools for exploring the properties of these nanomaterials, he uses Raman scattering techniques combined with optimized growth conditions for arc, CVD, and laser vaporization.

Andrew Rinzler

Dr. Andrew Rinzler received his bachelor's degree in Physics from the University of Bridgeport and his Ph.D. from the University of Connecticut in 1991. Upon graduation, he took an NRC postdoctoral fellowship at a small Army Research Lab (ARDEC) in Dover, New Jersey, where he studied the fracture surfaces of energetic materials using atomic force microscopy. From 1994 to 1998, Dr. Rinzler collaborated with Dr. Rick Smalley at Rice University on efforts to make, purify, understand, and exploit the truly novel properties of carbon nanotubes.

Dr. Rinzler has been an associate professor in the Department of Physics at the University of Florida since 1998, where he continues to pursue his interest in nanotubes and their applications. He has made many discoveries based on the exploitation of nanoscale materials for scientific and technological gain, particularly with respect to electronic and optical properties.

Dr Rinzler has found, for example, that polarized Raman spectra on fibers of aligned nanotubes led to the inference that light polarized perpendicular to the nanotube axis is not absorbed. Exploiting the angular dependence of the resonance Raman, his group developed a technique for quantifying the degree of orientation in aligned nanotube samples, a method that is now widely used for that purpose. Dr. Rinzler has developed a method for coating the probe tips with a stabilizing, insulating polymer, including being able to remove the polymer from the very tip of the nanotube; he hopes to exploit this method for developing bioelectrochemical probes with robust nanoscale imaging capabilities. Moreover, he has generated methods to make thin, pure nanotube films that simultaneously exhibit high electrical conductivity and high optical transmittance, properties that make the nanotubes potential competitors for ITO as transparent conductors. Most recently, Dr. Rinzler has developed a new nanotube-based transistor architecture that, along with the applications of the transparent nanotube films, provides the present focus of his group's research.

Traveling Team Members

Other team members traveling with the group included sponsors Kevin Lyons (NSF) and Kershed Cooper (ONR), as well as Masanobu Miyahara (WTEC) and Gerald Hane (Q-Paradigm).

APPENDIX B. SITE REPORTS

Site Visited:	**Advanced Industrial Science and Technology (AIST)** **1-1-1 Higashi, Tsukuba** **Ibaraki-ken 305-8565** **Japan**
Date Visited:	September 28, 2006
WTEC Attendees:	P. Ajayan (report author), P. Eklund, A. Rao, B. Pradhan

Hosts:	Dr. Morio Yumura, Senior Chief Scientist, Research Center for Advanced
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	Dr. Kenji Hata, Senior Research Scientist and Group Leader
	    Phone: +81-298-61-4551, E-mail: kenji-hata@aist.go.jp

BACKGROUND

The National Institute of Advanced Industrial Science and Technology (AIST) is an important laboratory for activities on SWCNTs, particularly in the light of their researchers' observations in recent years that vertically aligned, long, single-walled nanotube structures (which they call *supergrowth* of nanotubes) can be made using water-assisted, chemical vapor deposition. Although the activities in the AIST group are directed by Sumio Iijima, our group was briefed by Dr. Morio Yumura. We also received a presentation by Dr. K. Hata, affiliate of both AIST and the Fujitsu Group. The Fujitsu Group is one of the leading electronics manufacturers in Japan, and it has ongoing activities related to the development of carbon nanotube interconnects.

RESEARCH AND DEVELOPMENT ACTIVITIES IN MANUFACTURING

The activities at AIST are mainly at the basic research level, although some of the breakthroughs reported in the lab in the last couple of years could lead to interesting commercialization of this material. Dr. Hata mainly talked about the group's activities on the supergrowth of single-walled nanotubes (vertically aligned single-walled and single-walled nanotubes on different substrates), starting from their original work published in *Science* (Hata et al. 2004). Here, the nanotubes are grown over substrates coated with thin catalyst layers; the CVD is assisted by controlled amounts of water vapor added to the chamber. Over the last couple of years, AIST researchers have maintained better control of nanotube growth, and they can control, within a range, the diameters of the nanotubes grown, single-walled vs. double-walled nanotube growth, and design and growth of various patterns and architectures. The WTEC team also visited their growth facilities, a very well-controlled CVD system, which is nearly fully automated. The substrates are continuously fed and retracted automatically by robotic-controlled arms that can deposit multiple nanotube samples daily. The hope is that the whole process can be made continuous, and substrate-grown nanotubes can be grown and assembled continuously in a scalable manner.

Fujitsu Group

The Fujitsu Group has been working for the last several years on the growth of vertically aligned multi-walled nanotubes. The group has published several papers in the field, and its main goal is to replace via interconnects (as replacement for copper beyond the 42 nm node) for microelectronic applications. Its researchers have focused on growing controlled dimensions of multi-walled nanotubes inside vias and over substrates. They have been investigating the electrical characteristics of these structures, including ways to decrease via resistance by considering different metal contacts at the ends. They use microwave-assisted CVD for their growth, since they need to develop processes that are CMOS-compatible. They have been able to decrease growth temperature below 600°Celsius, but that is still above what would be practical for

integration with semiconductor processing. They showed impressive scalability of their approach with a sample of 300 mm silicon wafers completely and uniformly covered with vertically aligned, multi-walled nanotube arrays.

APPLICATIONS AND COMMERCIALIZATION

The two main activities that were presented during the WTEC visit to AIST were of differing commercial potential. In both cases, bulk manufacturing of nanotubes was not discussed. The two approaches (the Hata approach and the Fujitsu approach) produced vertically aligned nanotube arrays (single-walled and multi-walled) on substrates. The applications were confined to device applications and related to microelectronics, energy devices, thermal management structures, etc. Scalability of this approach was demonstrated. Some of the issues related to contacts (especially for via application) were discussed.

SUMMARY

The visit to AIST demonstrated two driving forces for Japanese interest in nanotubes. First, progress has been made in the growth of vertically aligned, substrate-grown nanotubes using the modified CVD process; much effort is being placed on this activity. Although this may not be the best way toward bulk manufacturing, this could produce an important material for device applications (electronics, sensors, energy devices etc.). Second, the electronics industry in Japan, in particular, Fujitsu, is clearly interested in looking at carbon nanotubes as an alternative material for future applications. One of the closest applications seems to focus on via interconnects where existing copper material is stated to have problems as the dimensions decrease below 50 nm.

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Site: **Institute of Physics, Chinese Academy of Sciences (IOP-CAS)**
                       P.O. Box 603
                       Beijing 100080
                       China

Date Visited: September 27, 2006

WTEC Attendees: A. Rinzler (report author), R. Blackmon, G. Hane, A.J. Hart, K. Cooper, K. Lyons

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                       Dr. Li Song, a recent Ph.D. graduate from Dr. Xie's group who gave a summary
                           presentation of the CNT research at IOP-CAS

BACKGROUND

The mission of the Institute of Physics, Chinese Academy of Sciences (IOP-CAS) is to conduct research in basic and technological sciences; to undertake nationwide integrated surveys on natural resources and ecological environment; to provide the country with scientific data and advice for governmental decision-making and to undertake government-assigned projects with regard to key problems in the process of social and economic development; to initiate personnel training; and to promote China's high-tech enterprises by its active involvement in these areas.

IOP-CAS forms one of the vertices of the triangular area comprising Beijing's "Silicon Valley" (the other two being Peking University and Tsinghua University). The IOP-CAS is partially funded by CAS, the Chinese National Science Foundation, and the Ministry of Science and Technology. There are 120 research staff members, 620 students, 71 support staff, and 32 administrative staff housed on a large campus comprised of at least ten modern buildings.

The technical activities of the institute are divided into the following subdisciplines: superconductivity; magnetism and magnetic materials; surface physics and electronics; optical physics and atomic and molecular physics; extreme condition physics; electron microscopy, vacuum and plasma physics; crystallography; nanomaterials science and technology; condensed matter theory and materials calculation; and finally, research and development.

The institute prides itself on a number of discoveries, including the YBCO (90K superconductor), advanced methods of solving crystal structures used worldwide in electron crystallography, and more recent advances in nanoscale science with numerous publications in leading peer-reviewed journals.

Since the 1970s, researchers in China have made remarkable progress, which, coupled with China's present economic boom and governmental support, can be said to have fully recovered and flourishing (Figure B.1).
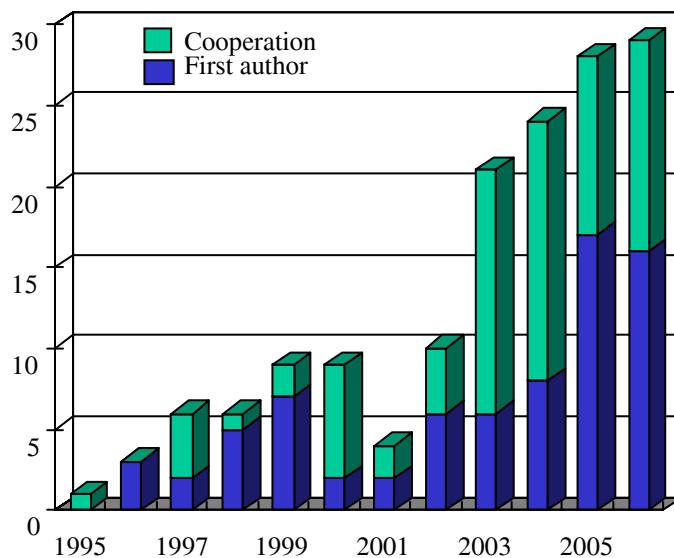
Figure B.1. Increase in publications in *Physical Review Letters*, *Science*, *Nature*, and the *Journal of the American Chemical Society* from 1995-2005.

CNT RESEARCH AND DEVELOPMENT ACTIVITIES

Our meeting took place in a large conference room followed by a brief presentation by Dr. Li Lu describing the history and scope of the IOP-CAS; Dr. Xie conducted the meeting. Dr. Sun presented results of initial experimental work on electrically driven water flow through SWCNTs. Dr. Rinzler gave an introduction to the WTEC study by giving a presentation reviewing the North American Workshop.

Dr. Xie's former student, Dr Li Song (soon to be a Humbolt fellow at one of the Kaiser Wilhelm institutes in Munich), and a current student, Ma Wenjun, gave technical presentations summarizing some of their work. Most of what was presented has already been published. They spoke on what they call "SWNT nonwoven" and "SWNT rings." Both of these are made by a similar CVD process in which a mixture of ferrocene and sulfur powder vapors from a first heated zone (52–95°C) are carried by an argon carrier gas with a small concentration of hydrocarbon feedstock (methane or acetylene) into the hot (1100°C) growth zone. In the case of the "SWNT nonwoven," the gas flow carries the nanotubes out of the hot zone to collect as an extended, somewhat uniform, deposit on the inside of the quartz flow tube, where the tube exits the tube furnace. This deposit, peeled as a film from the wall of the tube, constitutes the "SWNT nonwoven." The SWNT rings are coiled SWCNTs that are 300–500 nm in diameter. These are formed in reasonably high yield by incorporating a step change (increase) in the diameter of the flow tube within the growth zone. The change in the flow velocity occurring at the step change in tube diameter induces vortex flow and turbulence in the gas flow that evidently causes the nanotubes to coil up into the rings.

The mechanical properties of the "SWNT nonwoven" material have been measured. There is an orientational anisotropy imposed on the deposited material by the gas flow direction. Along the direction perpendicular to the flow direction, the films tear relatively easily. However, parallel to the flow direction, they measured the apparent elastic modulus ("apparent" because the cross-sectional area of the low density film was used in the calculation) of 188 GPa and a failure strength of 144 MPa. With the true cross-section considered, institute researchers estimate a value for the elastic modulus of 720 GPa. Electrical properties have also been measured with a 200 nm thick film showing a sheet resistance of 20 ohms/square.

Applications being explored for these films are transparent electrodes, electron field emitters, laminate composites (laminated with PEEK, the composite films showed a 40% increase in elastic modulus and 4% increase in fracture strength over pure PEEK) scaffolds for biocell proliferation and battery and fuel cell applications. No specifics regarding battery applications were given. Regarding the fuel cells, I explained the

result from Carbon Nanotechnologies, Inc. (CNI) that SWCNTs permit a 50-fold reduction in the precious catalyst content of the anode. Dr. Xie commented that fuel cells had numerous other problems to be solved before the CNI result would be of use, suggesting that they have postponed such nanotube applications until the other issues are solved. It did not seem that any of these applications were close to commercialization.

The SWNT rings were investigated for their field emission properties, but these are mainly of academic interest currently.

Dr. Xie estimated that funding since 1996 for nanotube research at CAS — including at IOP, the Institute of Mechanics (IOM) in Shenyang, the Institute of Organic Chemistry in Chendu, and the Institute of Chemistry in Beijing — was approximately $50 million, and that its manpower in CNT research over that period was approximately 200-300 [which must include students]. We did not have time for a tour of the facilities.

Issues

The growth process of the "SWNT nonwoven" is very slow for the amount of material that can be produced. Unless CAS scientists can dramatically accelerate this process, none of the technological applications being explored will be feasible with this material.

SUMMARY AND CONCLUSIONS

The IOP-CAS is a world-class research institution. Its mandate is predominantly focused on basic research, but it is beginning to diversify into applications.

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Site:	**Kaneko Research Lab**
	Molecular Chemistry Group
	Chiba University
	China-shi, Chiba, 263-8522
	Japan

Date Visited:	September 29, 2006
WTEC Attendees:	B. Pradhan (report author), A. Rao, P. Ajayan, P. Eklund
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BACKGROUND

Professor Kaneko has led the Molecular Chemistry Group at the Kaneko Research Lab since 1986. His main focus is studying gas adsorption on nanoporous materials, particularly nanoporous carbons, with a variety of unique techniques developed by his group over a period of time. Currently, there are 35 members in this group. The Japanese government and private industry provide funding.

This group has developed new characterization methods and analyses for nanoporous carbons and elucidated adsorption sates of molecules and ions. They applied molecular and solid state sciences to adsorption to develop carbon nanospace molecular science. For example, this group developed helium adsorption ultramicroporosimetry at 4.2 k for nanoporous carbon of less ordered structures, such as activated carbon fiber, *in situ* x-ray diffraction for determination of molecular structures confined in carbon nanospaces, *in situ* small angle x-ray scattering for adsorbed state analyses of molecules confined in carbon nanospaces and the superwide pressure range adsorption technique from P/P0 =10 E-9 for determination of ultramicroporosity. Professor Kaneko has tried to understand more precisely both carbon nanopore structures and adsorption processes on nanoporous carbons with the aid of GCMC (grand canonical Monte Carlo) simulation. These studies have been helpful to design a better activated carbon.

Recently, Professor Kaneko proposed a new concept of hydrophobicity gain of water on adsorption in hydrophobic carbon nanopore, showing the importance of water clusters. In 1999, he started to study ionic solutions (nanosolutions) confined in carbon nanospaces with extended x-ray absorption fine structure (EXAFS), showing that the hydration number around an ion decreases remarkably in the carbon nanospaces. The studies on nanosolution provide an indication for designing studies of molecules and ions confined in nanospaces of single-wall carbon nanotubilites such as SWNHs. The group clearly showed the relationship between adsorption properties and nanopore structures of carbon nanotubilites for H_2, CH_4, etc. Very recently, this group showed, experimentally and theoretically, that single-wall carbon nanotubilites exhibit a marked quantum molecular sieving effect for H_2 and D_2 on a SWNH.

This research is strongly associated with clean energy technology, such as methane storage, hydrogen storage and supercapacitor devices. Also, these are quite helpful to designing new nanostructured carbons for environmental and separation technologies. During the WTEC team's visit to Prof. Kaneko's lab, he presented his results focusing mainly on gas adsorption (H_2 and water) of single-walled carbon nanohorns, both experimental and theoretical.

Professor Kaneko has published more than 340 papers in international journals and was invited to 27 international conferences as plenary lecturer, keynote speaker, and invited speaker.

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BACKGROUND

Iljin Nanotech was formed in 2001 as an investment/diversification by Iljin Diamond. The company's headcount is 15 and includes four Ph.D.s. The mission statement of Iljin Nanotech is to be the world's leading supplier of high-quality carbon nanotubes. Iljin Nanotech executives envision selling both CNTs, as the company currently does, and in the future, CNT-enabled applications.

The parent company, Iljin Group, was founded as a corporate entity in 1967. Total annual revenue exceeds $900 million. Areas of activity include

- Industrial synthetic diamonds
- Copper foils
- High-voltage transformers
- Alloy and metallic parts
- Common electronics cables
- Heavy industry
- Light metals
- Carbon nanotubes

Initial startup funds for Iljin Nanotech were $2.4 million from Iljin Group. In 2003, the group gained additional funding through Korean government programs for the development of new light sources ($2 million/five-year programs) and FED displays ($1.4 million). Both of these government programs were structured as 75% government funding (from the Department of Commerce, Industry, and Energy) and 25% corporate matching from Iljin. To date, Iljin Nanotech has received a total of $5.8 million. The company's efforts are supported with process knowledge and IP from Professor Cheol-jin Lee in Korea (Kunsan University), and financial backing from Iljin Group.

Iljin Nanotech's facility is located in Gayang Techno Town, Gangseo-Gu, Seoul, Korea. The facility is a technology company incubator area.

Iljin Nanotech uses arc processing and CVD processing (in a tube-type furnace). The tube furnace is capable of a total annual output of MWCNTs at five-ten tons/year (on a continuous operating basis). Iljin Nanotech uses mixed metals for catalysts in its arc process and supported mixed metals for the catalyst in the CVD process. In general, Iljin Nanotech views their catalyst and carbon source as proprietary to their operations.

Iljin Nanotech is willing to submit a sample to WTEC for independent analysis if the analytical results are shared with Iljin Nanotech. Iljin Nanotech is also willing to accept product returns from clients if the client is able to demonstrate shortcomings with the product delivered.

In terms of occupational safety, the production systems at Iljin Nanotech are equipped with typical laboratory protocol (fume hoods) for the production devices. More sophisticated safety measures will be evaluated as the process is scaled-up.

RESEARCH AND DEVELOPMENT ACTIVITIES

Iljin Nanotech is currently focusing on research to control the quality of the tubes, with specific focus on controlling the number of walls produced and uniformity of walls in its multi-walled process. The desire is to produce a higher content of SWCNT in the CVD process. From its internal R&D budget, 70–80% of funding is spent on developing the growing techniques, while 20–30% of its funding is spent on investigating post-processing techniques for purification or fictionalization.

Areas of patent activity indicative of previous R&D efforts include

- Manufacturing method of carbon nanotube FED element using minute hole (Korea)
- Manufacturing of FED using selective growth of carbon nanotubes (Korea)
- Manufacturing of array of photo-device using selective growth of carbon nanotubes on silicon substrate (Korea)
- Manufacturing of vertical switching device using carbon nanotubes (Korea)
- Manufacturing of vertical switching device using selective growth of carbon nanotubes (Korea)
- Manufacturing of micromesh using silicon substrate (Korea)
- Manufacturing of electrode of nickel-carbon nanotube secondary battery using carbon nanotubes (Korea)
- Method of synthesizing carbon nanotubes in the multistage bipolar alumina mould and application of carbon nanotubes synthesized by that method (Korea)
- Tripolar electron emitting device using carbon nanotube manufacturing method of that device, flat panel display using that device, and method of synthesizing carbon nanotubes in bipolar oxidized alumina mould (Korea)
- Synthesis process of carbon nanotube and belt-type thermal CVD apparatus for that process (Korea)
- Multi vacuum chamber plasma CVD apparatus and the synthesis process of carbon nanotubes using that apparatus (Korea)
- Belt-equipped, low-temperature thermal CVD apparatus and the synthesis process of carbon nanotubes using that apparatus (Korea)
- Supercapacitor using electrodes made of new material (Korea)
- Manufacturing method of carbon nanotube (U.S., Europe, Japan, Korea)
- Low-temperature thermal CVD apparatus, and low-temperature synthesis of carbon nanotube using that apparatus (U.S., Europe, Japan, China, Korea)
- Gaseous phase purification of carbon nanotube by thermal treatment in diffusion furnace (U.S., Europe, Japan, China, Korea)
- Rotary electrode plasma apparatus and synthesis method of carbon nanotubes using that apparatus (Korea)
- Method to open the tip of carbon nanotubes and purification of carbon nanotubes (U.S., Europe, Japan, China, Korea)
- Synthesis of carbon nanotubes by low pressure CVD process (Korea)
- FED device using carbon nanotubes, and manufacturing method of that device (U.S., Europe, Japan, China, Korea)
- FED device using vertically aligned carbon nanotubes, and manufacturing of that device (U.S., Europe, Japan, China, Korea)
- Synthesis of carbon nanotubes by plasma CVD process (Korea)
- Manufacturing method of FED using carbon nanotubes (Korea)
- Mass purification process of carbon nanotubes (U.S., Europe, Japan, China, Korea)
- Mass synthesis method of high-purity carbon nanotubes vertically aligned on a large-scale substrate by thermal CVD process (U.S., Europe, Japan, China, Korea)

- Low-temperature synthesis of carbon nanotubes using catalytic metal membranes for decomposition of the carbon source gas (U.S., Europe, Japan, China, Korea)
- White light source using carbon nanotubes, and its manufacturing method (U.S., Europe, Japan, China, Korea)
- Synthesis process of high-purity carbon nanotubes
- Field emitter using carbon nanotubes (U.S., Europe, Japan, China, Korea)
- The method to regulate the diameter of carbon nanotubes using minute patterns of catalytic metal
- Arc discharge apparatus with revolving electrode, and carbon nanotubes synthesis process using that apparatus
- CVD apparatus, and carbon nanotubes synthesis using that apparatus (U.S., Europe, Japan, China, Korea)
- Vapor phase growth apparatus for synthesis of carbon nanotubes or carbon nanofibers, and synthesis process using that apparatus (Korea)
- Synthesis process of carbon nanotubes, and apparatus used for that synthesis (Korea)
- Manufacturing method of electrodes for high-output supercapacitors using carbon nanotubes, and supercapacitors using those electrodes (Korea)
- Purification process of single-walled carbon nanotubes, and heat treatment equipment used for that process (Korea)

The company has applied for a total of 49 patents, as shown in Table B.1:

Table B.1. Patents

Patents	**Korea**	**US**	**Japan**	**EU**	**China**
Applied	49	15	15	15	15
Granted	36	2	1	---	---

THE NANOTECHNOLOGY R&D CENTER

The Nanotechnology R&D Center was founded on February 22, 2000, as the laboratory attached to Iljin Nanotech Co., Ltd. Its mission is to be the world's best carbon nanotube R&D center. It has established a joint research system with carbon nanotube researchers from inside and outside of the country. It seeks to be the world leader for advanced material. Based on the research activities it has completed, Iljin has applied for 60 patents from Korea and other countries and has conducted government research projects in collaboration with leading research institutes in Korea. Hereafter, the Nanotechnology R&D Center will expand its research field in order to be the foundation stone for national competitive power in the area of advanced material (www.iljincnt.com).

Fields of Research

- Mass production of carbon nanotubes
- Growth of carbon nanotubes vertically aligned on the substrate of Si, SiO_2, Al_2O_3
- Growth of high-purity carbon nanotubes on large substrates
- Low-temperature growth of carbon nanotubes vertically aligned on glass or SiO_2 substrate
- Purification and structure control of carbon nanotubes
- FED and white light source using carbon nanotubes
- Electron emitter using carbon nanotubes
- Electrode of secondary battery using carbon nanotubes
- Fuel cell using carbon nanotubes
- Capacitor using carbon nanotubes
- Composite using carbon nanotubes
- Chemical compound using carbon nanotubes

SUMMARY AND CONCLUSIONS

To date, commercial profitability eludes CNTs. Emerging applications should boost the demand for CNTs. Iljin anticipates 30 tons/year applications emerging within one year. Applications for thin films are still three to four years from being realized. Iljin management believes that all of the tools for successful scale-up already exist; the limiting factor for scale-up is the demand required by applications.

Please note that although Iljin Nanotech primarily appears to be a bulk CNT supplier, a significant portion of its funding is chartered for the development of CNT applications.

Iljin Nanotech's presentation of its products is summarized on its website and in Table B.2.

Table B.2. High Quality, High Value, Competitive Price, Just in Time

Process	CNT Type	Product	Purity(%)		Diameter( )	Length( )	previous name
			vol %	wt %			
Arc-discharge Process	SWNT	ASA-100F	40	30	1~1.2(~10)	5~20	Arc SWNT AP(F)
		ASA-100Y	40	30	1~1.2(~10)	5~20	Arc SWNT AP(Y)
		ASP-100F	90	60~70	1~1.2(~10)	5~20	Arc SWNT PU
	MWCNT	AMI-200H	40	20	10~20	3~7	Arc MWCNT IC(H2)
CVD Process	MWCNT	CM-95			10~15	10~20	CVD MWCNT 95
	Thin MWCNT	CMP-310F	95	95	3~5	10~20	CVD MWCNT R
		CMP-320F			4~6		
		CMP-330F			4~7		
		CMP-340F			6~9		

Source: www.iljinnanotech.co.kr/en/home.html.

REFERENCES

Iljin Nanotech website, www.iljincnt.com (accessed on November 7, 2006).

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BACKGROUND

Nano Carbon Technologies Co., Ltd. (NCT), was founded in April 2006 as a joint venture between Hodogaya Chemical Co., Ltd., and Mitsui Co., Ltd. Its 40 employees are primarily engaged in the manufacturing of MWCNTs and MWCNTs containing composites. Dr. Shinji Kurihara oversees its annual operating budget of 2.5 billion yen (66% Hodogaya Chemical; 34% Mitsui). NCT has been very successful with the production of MWCNTs using a floating catalyst CVD pioneered by Prof. Morinubo Endo of Shinshu University.

A schematic of NCT's floating catalyst CVD process is shown in Figure B.2. The feed containing hydrocarbon and catalyst are decomposed into "bulk grade" MWCNTs inside a reactor which typically operates at 700°C (Figure B.2). The bulk MWCNTs are subsequently processed through two high-temperature ovens (typical operation temperature, 2600°C) to remove the residue metal catalyst particles and anneal structural defects present in the bulk MWCNTs. The final products are harvested either as "high-purity grade" MWCNTs (99.5 wt. % carbon), or mixed with appropriate resins to prepare high-purity MWCNTs containing composites. An average high-purity MWCNT production capacity is a few kilograms/hour, and typical structural and physical properties are listed in Table B.3.
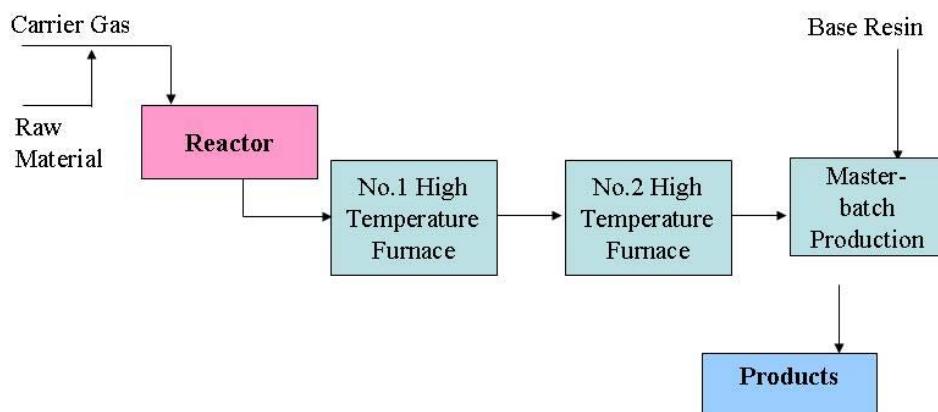
Figure B.2. Schematic of the floating catalyst CVD method.

Table B.3. Summary of Structural and Physical Properties of High-Purity MWCNTs

Property/Dimension	Value	Measuring Method
d (002) (nm)	0.3385	d(002) and L_c(002) is interlayer spacing from XRD
L_c (nm)	13	
Diameter (nm)	40-90	Diameter and length of tubes were determined by FE-SEM observation
Aspect ratio	> 100	
Bulk density (g/cm^3)	0.005	Volume density is measured by bulk density measuring method.
Real density (g/cm^3)	2.1	Real density is measured by a pycnometer
Specific surface area (BET) (m^2/g)	28	Specific surface area is measured by N_2 adsorption
Burning temperature	600	Nanotubes are oxidized in an air atmosphere using TGA.
Metal impurity	< 450 ppm	X-ray fluorescence spectroscopy was used to determine metallic impurities.

Comparison of Structural Properties of Bulk and High-Purity MWCNTs

The quality of the MWCNTs produced by NCT was determined primarily using Raman spectroscopy, x-ray diffraction, and high-resolution transmission electron microscopy (HRTEM). Nearly all MWCNTs exhibit a uniform core diameter of 5 nm. Consistent with this picture, the ratio of the intensity of the disorder band (D-band) to that of the graphite band (G-band) decreases from 0.97 to 0.07 upon annealing the bulk-grade MWCNTs (Figure B.3b) and the (002) x-ray diffraction peak sharpens significantly (Figure B.3a). The relatively poor structural order in the walls of the bulk-grade MWCNTs exhibits a dramatic improvement upon annealing (Figure B.4).
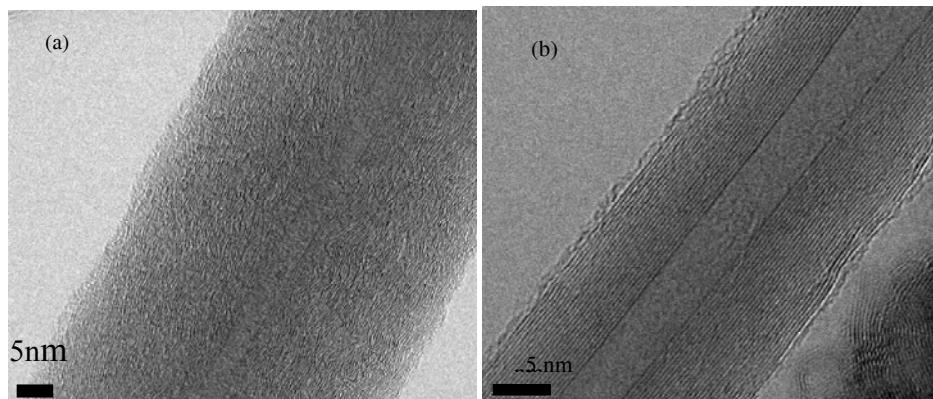
Figure B.3. Comparison of HRTEM images of (a) bulk- grade; (b) high-purity-grade MWCNTs (Courtesy of Dr. Kim of Shinshu University).
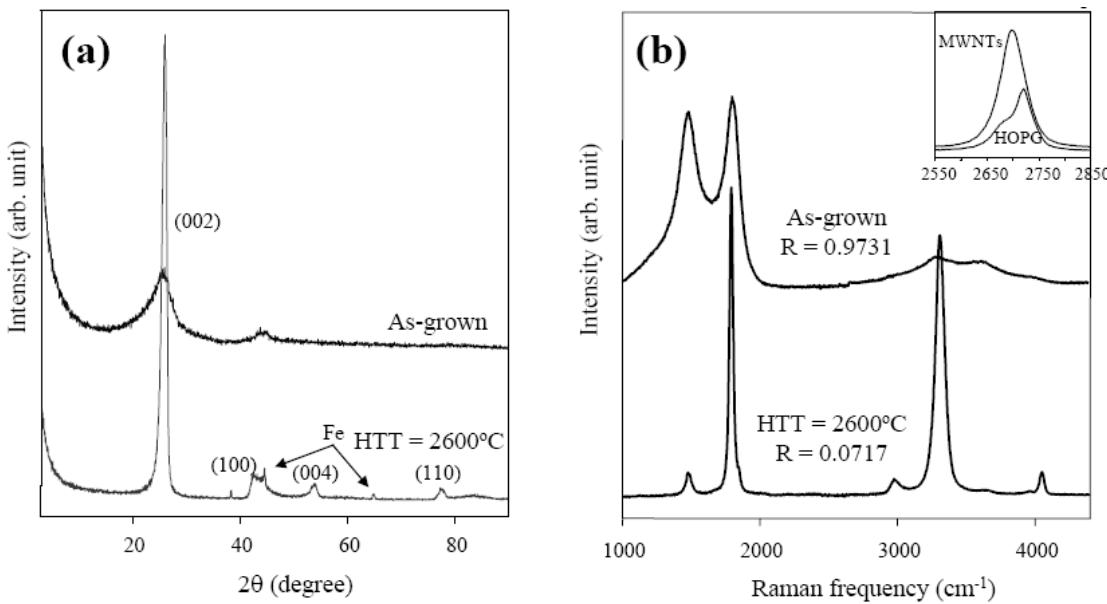
Figure B.4. The XRD (a) and Raman spectroscopy (b) both indicate a dramatic improvement in structural order and residual catalyst impurity in annealed MWCNTs (Courtesy of Dr. Kim of Shinshu University)

Aside from manufacturing high-purity MWCNTs, NCT has also prepared and tested MWCNTs containing composites for electrostatic discharge and biological applications. MWCNTs were incorporated into polycarbonates and epoxies, and the resulting composites showed enhanced physical and electrical properties as compared to commercially used composites. A maximum MWCNT loading of 5 wt. % was achieved. It is noteworthy that the annealed MWCNTs (which contain a very low percentage of residue catalyst) are proving to be useful in biomedical applications. A summary of bio-related activities at Nano Carbon Technologies Co., Ltd., is shown in Table B.4.

Table B.4. Results of experiments conducted by NCT suggest that MWCNTs with very low residual catalyst exhibit low or no toxicity

Test Methods	Objectives	Institution/Lab	Results
Agar Diffusion Test ISO10933-5,1999 ISO10993-12,2002 ISO/IEC17025,1999	In Vitro Cytotoxicity (Cellular degeneration & malformation)	TOXIKON Corporation, MA, USA	No biological reactivity
Skin Irritation ISO10933-5,2002 ISO10993-12,2002 ISO/IEC17025,1999	Primary dermal irritation	-ditto-	Negligible irritant
Klingman Maximization ISO10933-10,2002 ISO10933-12,2002 ISO/IEC17025,1999	Induction/ Intradermal allergenic potential or sensitizing capacity	-ditto-	Not significant (= control)
Mouse test (1)	Immunological evaluation with T-Cell(CD4/CD8), pathological	Shinshu Univ, med-school	Not significant (= control)
Mouse Test (2)	-ditto- , confirmation of the reproducibility	-ditto-	-ditto-
Mouse Test (2)(Additional)	Cytokine evaluation	-ditto-	-ditto-
Broader biological evaluation (1)	Preliminary Tests	A national lab	No toxicity

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BACKGROUND

The National Center for Nanoscience and Technology (NCNST) was established in December, 2003, with the Chinese Academy of Sciences (CAS), Peking University, and Tsinghua University as its initiators and co-founders. NCNST goals are as follows:

- Public technology platform (nanofabrication and characterization services)
- Promoting new fronts of nanoscience
- Establishing database
- Consultation to government and industry
- Education and training of young scientists
- Promoting government-institution-industry linkage
- Windows for international collaboration

NCNST's Specific Mission

- *Nanofabrication and nanodevice*: Focus on nanofabrication and assembly, develop relevant tools, and explore fundamental research on conceptual and prototype nanodevices for electronics, optoelectronics, and molecular devices
- *Nanomaterials and nanostructure*: Place emphasis on developing advanced synthesis methods and fabrication equipment for nanomaterials and nanostructures with tailored functionalities
- *Nanomedicine and biology*: Exploit principles and technologies of nanoscience to develop novel detection methods and devices in medicine and life sciences
- *Structure and function characterization*: Establish world-class characterization metrology for nanomaterials and nanostructure to develop advanced methods and instruments for characterizing nanostructures and functions

NCNST is funded at a level of US$32.5 million from the National Development and Reform Commission (NDRC). It has a scientific and administrative staff of 155. A large new building is scheduled to be completed in 2008.

In March 2005, The National Technical Committee on Nanotechnology of the Standardization Administration of China was established at NCNST after approval from the Standardization Administration of China. Therefore, the NCNST is responsible for organizing and implementing nanotechnology standards in China.

CNT Research and Development Activities

The WTEC team's meeting at NCNST took place in a conference room in the temporary facilities of the NCNST (while their new building is under construction). Dr. Zhang gave two presentations, one focusing on the mission and administration of the center, and the other focusing on some of his technical activities. The

latter concerned improved structural and wear-resistant polymer composites through loading with a wide variety of nanoparticles including fullerenes, silica nanospheres, and TiO_2 nanoparticles, with plans to move into carbon nanotubes. Carbon nanotube-related efforts comprised one micrograph showing MWCNTs reasonably well-dispersed at a 5% loading within a polycarbonate matrix.

Before moving on to NCNST, Dr. Zhang was an Alexander von Humboldt Research fellow at the Institute for Composite Materials (IVW), Germany. While there, he obtained the Sofja Kovalevskaja award from the Humboldt Foundation. The award granted him one million euros to establish an independent research team at the IVW. The objective of the award project was to focus on the long-term behavior (e.g., creep, fatigue, and tribological properties) of short fiber/nanoparticle-reinforced polymer composites at various environmental temperatures, with the goal of leading to an accelerated use of these materials in various industrial applications. With this prior experience, the new facilities of the center, and the close contacts of the center with nanotube researchers (e.g., Prof. Sishen Xie and Prof. Lianfeng Sun), Dr. Zhang is positioned to make significant headway in structural nanotube composites.

SUMMARY AND CONCLUSIONS

Charged with the implementation of nanotechnology standards in China, the NCNST could become an important institution for developing the much needed assays of nanotube purity and quality in China.

REFERENCES

National Center for Nanoscience and Technology website, www.nanoctr.cn/e_index.jsp (accessed on May 15, 2007).

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BACKGROUND

The research laboratory of NEC Corporation is where modern nanotube research started. Sumio Iijima is credited to be the first person who discovered nanotubes in 1991 at NEC. NEC is one of the major Japanese companies in electronics, and it has several laboratories all over the world; its center is at the Tsukuba location. Dr. Masako Yudasaka was our main contact.

RESEARCH AND DEVELOPMENT ACTIVITIES IN MANUFACTURING

Not many research activities on manufacturing of single-walled or multi-walled nanotubes exist at NEC at present. The only relevant activity to the WTEC team's mission was the production and application of single-walled carbon nanohorns (SWNH), which are relatives of SWNT (Figure B.5). These have single-layered, closed-shell graphene structures, like SWNTs, but with much smaller aspect ratio and often non-uniform shapes. The main characteristic of SWNHs is that it takes approximately 2000 of them assembled to form a robust aggregate (a secondary particle) of about 100 nm. They provide porous structures with large surface areas. SWNHs can be made by laser ablation at hundreds grams/day. We were shown the laboratory that housed the synthesis system. Compared to SWCNTs, SWNHs are expected to become a low-cost raw material.

One research group at NEC focused on the theory of hot-carrier dynamics in SWCNTs. Other groups worked on SWNT applications, though group members were not introduced due to time limitations and the need to protect corporate secrets, particularly in the nanotube area.
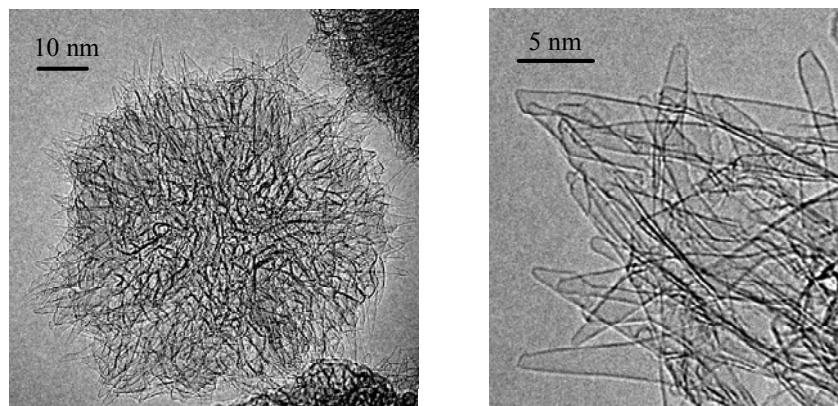
Figure B.5. Typical structure of single-walled carbon nanohorns.

APPLICATIONS AND COMMERCIALIZATION

NEC seemed interested in areas such as energy and health in addition to its mainstream electronics. The applications of SWNHs are related to fuel cells; SWNHs are used as electrodes units. Light weight, large surface area, and thermal stability make SWNHs useful for such use. Other applications of SWNHs could be in composites and supercapacitors, which are currently invested, but have not yet reached the commercial level. On the other hand, due to the success of the large-scale production of SWNHs, NEC representatives said that they will make a sale of SWNHs before 2008.

SUMMARY

The WTEC team's NEC hosts did not show the recent activities on SWCNTs except for a very basic one; however, SWNHs seem to have various interesting applications, which are attractive due to their ease of manufacturing and lower cost in comparison to SWCNTs.

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                             China

Date Visited: September 27, 2006

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BACKGROUND

The College of Chemistry and Molecular Engineering at Peking University, founded in 1910, was the first chemistry department in China. It is currently the biggest chemistry education and research institute in China. The facility houses departments for inorganic chemistry, physical chemistry, polymer chemistry, and physics, organic chemistry, and analytical chemistry — all of which have been appointed key majors by the Chinese Ministry of Education (MOE).

The College of Chemistry and Molecular Engineering is currently divided as follows: State Key Laboratory for Structural Chemistry of Unstable and Stable Species; State Key Laboratory of Rare Earth Materials Chemistry and Applications; MOE Key Laboratory of Bio-Organic and Molecular Engineering; Analysis and Test Center of Peking University; Experimental Chemistry Center of Peking University; and Center for Nanoscale Science and Technology (CNST) of Peking University.

The College of Chemistry and Molecular Engineering now has a large number of faculty and staff members, including eight members of the Chinese Academy of Sciences (academicians), 12 Changjiang professors, 55 professors, and 60 associate professors.

WTEC panelists toured the laboratory facilities at Peking University to gain insight into the type and quality of technology related to carbon nanotube research housed within the department (Figures B.6, B.7, B.8, B.9, and B.10).

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[3] "Peking" University is the English translation of "Beijing" University chosen by the host institution.

Figure B.6. Equipment and instrumentation used in conjunction with CNT research at Peking University Laboratory of Dr. Zujin Shi, Associate Professor, Inorganic Chemistry, Carbon Cluster Materials.

Figure B.7. Laboratory of Prof. Zhongfan Liu and Prof. Jin Zhang, Peking University College of Chemistry.

Figure B.8. CVD furnace (fabricated in-house — quartz tube) used to perform experiments related to growth characteristics and fluctuations of reaction temperature.

Figure B.9. Commercially procured CVD tube furnace with integrated atmosphere control.
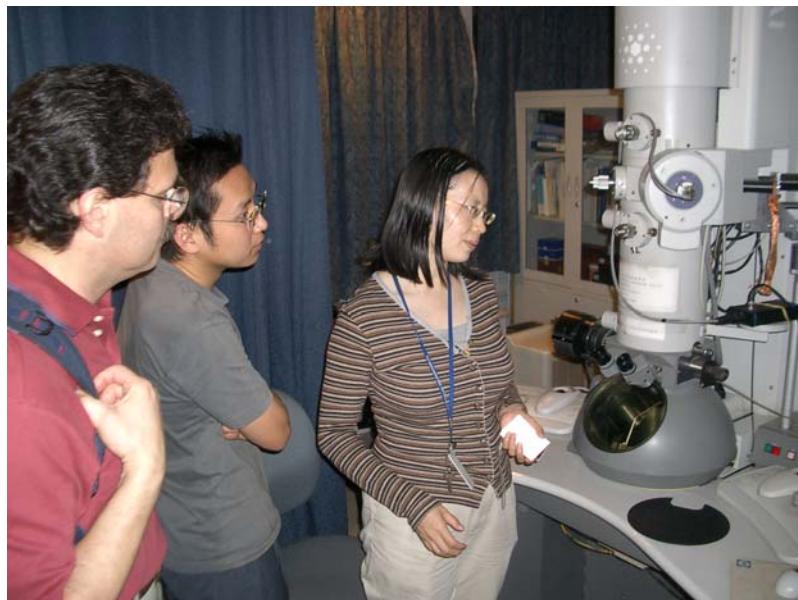
Figure B.10. Laboratory and research interest of Dr. Jingyun Wang, Peking University, School of Electronics Engineering and Computer Science.

RESEARCH AND DEVELOPMENT ACTIVITIES

Facilities

The College of Chemistry is well-equipped for research and educational purposes.

NMR Spectrometer

- ARX-400 NMR Spectrometer (Spectrospin Switzerland)
- NMR-YH200 NMR Spectrometer (Varian)

HPLC System

- HP1100 HPLC System (Agilent Technologies) (8)
- HP1090 HPLC System (Hewlett-Packard)

- The Waters Delta 600 system (Waters) (4)
- Waters 600E Multisolvent Delivery System (Waters) (2)
- The Waters 820 system (Waters)
- Gilson 322-H2 HPLC Pumps (Gilson)
- Waters Breeze HPLC System 1525

X-ray Facilities

- DMAX 2400 X-Ray Diffractometer (Rigaku, Japan)
- D8 Discover with GADDS, X-ray Diffraction (Bruker) (2)
- X'Pert PRO diffraction system (Hewlett-Packard)
- MultiFlex x-ray diffraction system (Rigaku, Japan)
- S4 Explorer x-ray fluorescence (XRF) spectrometer (Bruker)
- Nonius Kappa CCD x-ray diffractometer system (Nonius B.V.)
- Bruker D8 Advance x-ray diffractometer (Bruker)

Atomic Force Microscope (AFM)

- Nanoscope IIIa atomic force microscope (Digital Instruments Corp.)
- AP-190 AFM microscope (Park)
- SPA3800 SPM (Seiko)

Gas Chromatography

- GCQ GC/MS (Finnigan Mat) (2)
- VG ZAB HS high-resolution mass spectrometer with GC (VG Analytical, Ltd.)
- HP6890 GC (Hewlett-Packard)
- HP6890 GC (Hewlett-Packard)

Other Instruments

- MagLab System 2000 magnetometer (Oxford, UK)
- PROFILE SPEC ICP-AES (Leeman Labs)
- Nicolet 910/750 Fourier Transform Raman spectrometer (Nicolet)
- ALV/DLS/SLS-5022F Laser Light Scattering Goniometer System (ALV)
- Renishaw Raman Microscope System 1000 (Renishaw)
- The Ramanor U1000 double additive monochromator (Jobin Yvon)
- FluoroLog-3 Spectrofluorometer (Jobin Yvon)

SUMMARY AND CONCLUSIONS

The Peking University College of Chemistry and Molecular Engineering houses a diverse group of researchers. A number of these researchers, including those mentioned in this report, have specialized in carbon nanotube growth, functionalization, manipulation (manipulated growth via nano lithography and etching), as well as visualization and measurement techniques.

The group does not appear to have a strategic core directive or investment to focus on carbon nanotubes. Developments and investigations related to CNTs that are generated within the department stem from the research interests of specific professors. It appears that the various professors are left to secure funding independent of the other related activities. Consequently, there exist discrepancies in funding between the various laboratories dedicated to investigation of CNTs. Despite the funding discrepancies, the various groups have each been able to perform high-quality research in their specific areas. A central organizing body and mission statement along with uniform funding of the researchers participating in the program would well serve Peking University.

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Web-based biography, Jin ZHANG, www.chem.pku.edu.cn/zhangj/eindex.htm (accessed on November 7, 2006).

Web-based biography, LI Yan, www.chem.pku.edu.cn/liy/eindex.htm (accessed on November 7, 2006).

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Date Visited: September 27, 2006

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BACKGROUND

The mission of RIKEN Frontier Research System (FRS) Nanoscience Research Program is to conduct comprehensive research in science and technology (excluding only the humanities and social sciences) and to publicly disseminate the results of its scientific research and technological developments. RIKEN carries out high-level experimental and research work in a wide range of fields, including physics, chemistry, medical science, biology, and engineering, covering the entire range from basic research to practical applications. RIKEN was first organized in 1917 as a private research foundation and reorganized in 2003 as an independent administrative institution under Japan's Ministry of Education, Culture, Sports, Science, and Technology (MEXT).

Approximately 88,000 million yen are spent on research and development. RIKEN has the Discovery Research Institute, the Frontier Research System, six strategic research centers in life science areas, and three research infrastructure centers with total personnel of 5,500, including 3,000 researchers. The Nanoscience Research Program, among nine programs at the FRS is a relatively recent effort, started in December 2002.

RESEARCH AND DEVELOPMENT ACTIVITIES

Nanoscience is viewed at RIKEN as a new concept for promoting interdisciplinary and collaborative linkage in research conducted at the nanoscale, and encompasses nanotechnology, a new and growing field identified as a major field of importance in the second-term science and technology basic plan (FY2001-5) promulgated by the Japanese government. With the completion of the Nanoscience Joint Laboratory on its Wako campus in February 2003, RIKEN established its flagship program for promoting leading-edge research in the field with the very latest high-tech devices and equipment. With the establishment of this program, RIKEN went immediately ahead in the selection of research projects from among candidates proposed by RIKEN scientists to form the nanoscience research team; an additional support organization, the Nanoscience Development and Support Team, has been created to provide technical and developmental assistance where necessary.

In order to most effectively promote this leading-edge research, the Nanoscience Research Team was established to use the Nanoscience Joint Laboratory. It is divided into 20 sub-teams, which are energetically pursuing their research goals using the most advanced equipment and methodologies to push the envelope in nanoscientific research, exploiting RIKEN's inherent research potential to the utmost.

Research Areas

RIKEN has been developing several novel technologies related to nanoscience and nanotechnology. Its main subjects are fabrication of nanoscale electrodes, high-aspect nanoimprinting, nanoscale processing technologies of super-hard or super-soft materials, nanoscale investigation of single molecules on metal and semiconductor surfaces, and nanoelectronics operation at ultralow temperature. RIKEN is promoting

collaboration with other research groups to discover advanced nanoscience and nanotechnology and also fabrication support for the various application requests. The RIKEN goal is to create new wave of nanotechnology research that will radically advance nanoscience research in Japan and in the world.

Research Subjects

- Fabrication of nanoscale electrodes and its applications
- High-aspect nanoimprint lithography and its applications
- Nanofabrication of special hard/soft materials and its applications
- Nanoscale investigation of single molecules on metal and semiconductor surfaces
- Nanoelectronics operation at ultralow temperatures and its applications

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RIKEN Nanoscience Research Program website, www.riken.jp/engn/r-world/research/lab/nano/index.html (accessed on November 8, 2006).

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BACKGROUND

The WTEC team visited the corporate R&D center of Samsung SDI. Samsung SDI is a division of the much larger Samsung Corporation, which produces a wide variety of consumer electronics, heavy equipment, and other products. SDI develops and manufactures displays ranging from mobile phone screens to large televisions; it is one of the largest producers of lithium-ion batteries, and it is researching new power and energy technologies, including small fuel cells. SDI has approximately 1000 employees at its R&D center and approximately 26,000 employees in all. In 2005, Samsung Corporation had sales of $140.9 billion (Samsung Group Annual Report 2005). The worldwide market for displays is $150 billion annually.

CNT RESEARCH AND DEVELOPMENT ACTIVITIES

SDI is developing a field emission display (FED) using CNTs as the field emission source. SDI has been developing the FED for six years, and currently 70-80 employees and 10% of the SDI research budget is dedicated to the project. SDI initially received funding from the Korean government to support the FED project.

The Samsung CNT FED is microfabricated on display glass and features a triode structure, where a bias voltage is applied between the bottom (cathode, ITO) and middle (gate) electrodes, and the emission is focused by the top electrode (Choi et al. 2006). The CNT emitters (there are dozens of emission "spots," each containing many CNT emitters, per pixel of the display), are applied to the device by screen-printing of a custom-made CNT paste, or by direct growth of CNTs by CVD. In the former case, commercially available CNTs are mixed with many ingredients, and the paste is wiped through a screen mask that is placed over the device (Choi et al. 2004). In the latter case, a catalyst layer (e.g., sputtered Ni) is deposited on the device, and the CNTs are subsequently grown by thermal CVD of CO/H_2 with catalyst deposited by sputtering. For screen printing of the paste, the maximum, and therefore limiting, process temperature is that of firing the paste after printing (<450°C); for CNT growth, the CVD temperature is limiting (lowest 420°C so far; must be <500°C to prevent melting of the glass). While isolated vertically aligned CNTs as grown by the CVD process are generally desired for field emission, the CNTs in the paste are generally tangled and parallel to the substrate. Therefore, CNTs as deposited by the paste method are aligned vertically by surface treatment (e.g., applying and peeling a tape from the substrate).

Owing to its versatility and scalability to large substrate areas, the paste method is preferred and is being pursued for current prototype development. Many types of CNTs (e.g., SWCNTs and MWCNTs of various diameters and lengths) obtained from many suppliers have been evaluated by this method. SWCNTs generally exhibit a higher field emission density yet lower lifetime, while MWCNTs exhibit lower emission density yet longer lifetime. Therefore, a careful tradeoff must be made to optimize device performance. Currently, uniform-length, high-quality, small-diameter MWCNTs are preferred (and MWCNTs are also easier to disperse than SWCNTs), and a price of less than US$10/gram would be suitable for commercial production of the CNT FED.

So far, SDI has made prototype CNT FED displays in the 5–37" range. The CVD growth process limits display size to the size of the CVD chamber; however, up to 70" displays can be made by the paste method.

The SDI development team identified many achievements and remaining challenges in the FED program. A main challenge related to use of CNTs in the display is the uniformity of emission. This is improved by adding a resistive layer under the CNT paste and may be further managed by independently adjusting (calibrating) the voltages over the array to give uniform emission. A lifetime of 30,000 hours is sought, and the SDI team believes this can be achieved using their technology. Also, as the display size increases, maintaining good vacuum sealing is an increasing challenge, and inadequate vacuum decreases the lifetime, as the emitters decay more quickly.

SUMMARY AND CONCLUSIONS

In general, CNTs are sought for field emission because of the high current density due to their high aspect ratio; however, there are many other candidate materials (e.g., small-diameter nanowires, diamond nanocrystals, nanofabricated metal tips) for structure-based and surface-based field emission.

In spite of these alternatives, the SDI team has made significant strides with its CNT-FED development effort and seems poised to bring the display to market within the next few years. The initial target market is 30–50" displays, while smaller displays will be of organic light-emitting diode (OLED) and liquid crystal display (LCD) types; larger displays will be plasma-type. Team members also anticipated continued development for one year and having a product on the market in two to three years.

While the WTEC study team is not aware of any other SDI projects that involve CNTs, it seems that the CNT paste technology may be a versatile platform for integration of CNT films into a wider variety of electronic devices.

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BACKGROUND

The team visited the NANO Systems Institute (NSI) at Seoul National University (SNU). The NSI is a National Core Research Center (NCRC) of South Korea, launched in 2003 in collaboration with Samsung Advanced Institute of Technology (SAIT) and Korea Institute of Science and Technology (KIST). The NSI seeks to realize nanoscale application systems based on technologies combined with scientific principles developed in various departments at SNU and also to deploy them as active member companies.

The NSI is funded with approximately $2.5 million per year, and its current plan is for seven years. The NSI staff has 24 SNU faculty members, 106 graduate students and post-docs, and over a dozen researchers at member organizations and collaborating academic institutions.

CNT RESEARCH AND DEVELOPMENT ACTIVITIES

There is a wide variety of CNT-related research within the NSI, and the study team was hosted by four faculty members who are working in these areas. The following is a brief summary of their CNT research:

Prof. Young June Park

- Integration of CNTs with microelectronic devices, where a standard CMOS architecture is fabricated and then a tangled film of CNTs is deposited on the device (e.g., in a recessed area of a MOSFET). This is sought for applications in gas sensing.
- Use of vertically aligned CNTs grown on CMOS architecture as an antenna. The CNTs are seeded in the pores of an anodic aluminum oxide (AAO) template.

Prof. Yong Hyup Kim

- Thermal CVD growth of MWCNT forests, where the process is tailored to achieve spatial uniformity of field emission.
- Development of a flat panel light source using CNT arrays as the cathode emitters.
- Development of metal and polymer nanocomposites containing CNTs.

Prof. Yungwoo Park

- Formation and characterization of individual polymer chains inside CNTs. This is recent work which will be published shortly in *Chemical Physics Letters*.

- Development of a CNT-based three-terminal relay, in collaboration with Chalmers University in Goteborg, Sweden (Lee et al. 2004). This features a single cantilevered CNT, which is electrostatically actuated.

Prof. Seonghoon Lee

- Synthesis and electrical and optical characterization of low-dimensional materials, such as semiconductor quantum dots and metal nanoparticles (0D), carbon nanotubes and nanowires (1D), and thin films (2D).

- Electrical and optical devices with low-dimensional materials such as CNT-FED, plastic solar cell, OLED, LD, white LED, and solid state lighting.

SUMMARY AND CONCLUSIONS

CNT research at NSI does not focus on synthesis of CNTs as materials alone; rather, it seeks to use CNTs as functional elements in devices such as sensors, relays, and displays. This approach fits with the broader goal of the NSI center for development and commercialization of microscale and nanoscale systems. Overall, much of the CNT work at NSI, especially devices based on CNTs integrated with the CMOS platform, is still in its early stages, so the WTEC team expects results to accelerate in the coming year.

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NSI website (English), nsi.snu.ac.kr/eng/main/main.php (accessed on May 15, 2007).

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BACKGROUND

In 2001 Shenzhen Nano-Technologies Port Co., Ltd. (NTP) began commercial production of carbon nanotubes. NTP produces up to 10 tons/year of SWCNTs and MWCNTs for industrial and institutional use. The production facility consists of multiple cycled vertical CVD tube furnaces (Figure B.11).

Figure B.11. Cycled CVD furnaces.

NTP primarily uses CVD processing (in multiple tube-type furnaces) as its main production technique for SWCNTs, DWCNTs, and MWCNTs. There are indications that NTP may use arc furnaces for SWCNT production. The 1100 square meter facility currently has an annual output of 10 tons/year (on a 1-shift/day basis). The facility is staffed by 20–40 employees. The employees conduct both research and production at the facility. Maximum instantaneous output is approximately 5 kg/hr (40 kg/day).

NTP representatives did not directly disclose the type of catalyst used; information on NTP's website indicated that the metal catalyst is likely a supported metal mixture of Fe, Ni, Co, Mo, etc. NTP is also directly marketing its nano metal and nano alumina as products. NTP is capable of producing more than 20 kg/day of catalyst. NTP utilizes a variety of carbon sources, including CO, CH_4 (methane), C_2H_6 (ethane), C_2H_2 (ethyne), natural gas, methanol, and ethanol for different products.

NTP derives different quality products from its process and markets tiered products based on the purity and degree of wall uniformity.

NTP is willing to accept product returns from clients if the client is able to demonstrate shortcomings with the product that has been delivered. To date, NTP has had less than five instances where a client has rejected a product due to suspect purity.

The level of occupational safety at NTP has not been assessed. The photographs available from its web material indicate a well-enclosed furnace operation in a relatively clean environment. Dedicated exhaust hoods are not apparent from the photograph.

NTP's facility does include some in-house instrumentation for testing of the nanotube purity and quality. TEM and SEM testing is performed at some universities and institutes.

RESEARCH AND DEVELOPMENT

Product development at NTP is focused on the control of the tube diameter and purity in the as-produced state. NTP is working to develop high-quality SWCNTs with DWCNTs and TWCNTs contained in the mix.

NTP's intellectual property position is not well understood. Information regarding patents, patent applications, and research is not available from its website. The company's intellectual property and process know-how are likely considered to be industry trade secrets.

SUMMARY AND CONCLUSIONS

NTP's presentation of its products is summarized on its website. NTP anticipates that a demand of more than 10 tons/year will allow the company to reduce pricing to $50 per kilogram in the near future.

REFERENCES

NTP CNT website, www.nanotubes.com.cn (accessed on May 15, 2007).

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BACKGROUND

The group at Shinshu University is headed by Prof. M. Endo and focuses on large-scale production of MWCNTs. Their synthesis approach is based on a modified catalytic chemical vapor deposition (CCVD) method pioneered by Prof. Endo for the growth of VGCFs (Figure B.12).
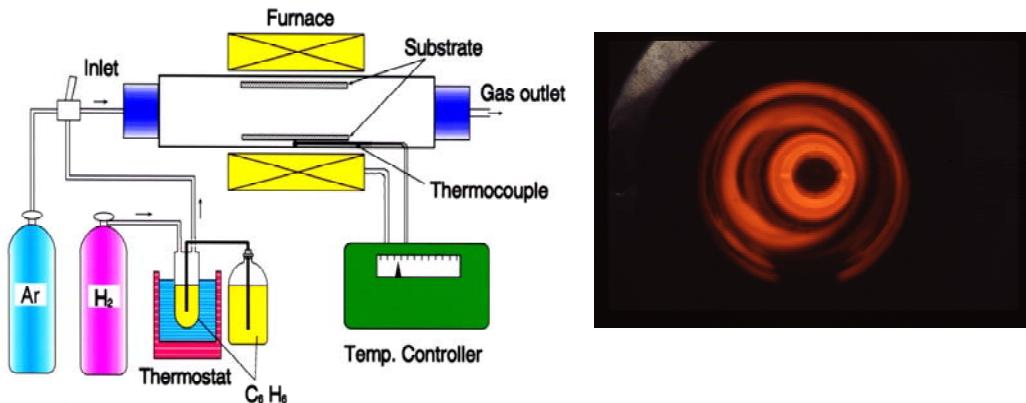
Figure B.12. (a) Schematic of the CVD setup for the growth of VGCFs (Oberlin et al. 1976); (b) photo of reactor describing the growth of thin fibers from Fe-seeded substrate surface by seeding method.
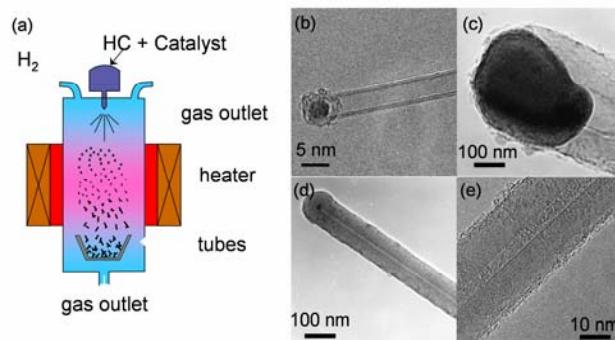
Figure B.13. (a) Schematic of the modified CVD setup for the floating growth of VGCFs (Endo1986; Endo 1988); (b-d) TEM images showing metal particles at the tip and continuous and small diameter hollow tube grown by Fe nanocatalytic particle; (e) TEM picture of the multi-walled CNT grown by floating Fe-catalyst.

The mass production of MWCNTs is achieved through a modified fluidized bed shown in Figure B.13a (Endo 1986; Endo 1988). The fluidized bed geometry permits better control of the catalyst-feed ratio and the

aspect ratio of the resulting MWCNTs (Figure B.13b-d). For example, the group's MWCNTs predominantly contain relatively smaller core diameter (~3-5 nm) with an average outer tube diameter of 40 nm (Figure B.13e).

Besides mass production of MWCNTs, the Shinshu group has also made significant advances in nanotube-based applications, ranging from efficient lithium-ion batteries (LIBs) to biocompatible microcatheters coated with MWCNT-nylon composite. A few of these applications are discussed below.

A systematic study of relative charge discharge capacity of an LIB using synthetic graphite anode as a function of weight-percent of MWCNTs is shown in Figure B.14. A "near-perfect" response was observed over 50 charge-discharge cycles using a composite graphite anode that contained 10 weight % MWCNTs. The MWCNTs were heat-treated to 2500°C prior to their use in the graphite anodes. The enhanced capacity is attributed to the increased resilience of the anode due to the presence of MWCNTs.
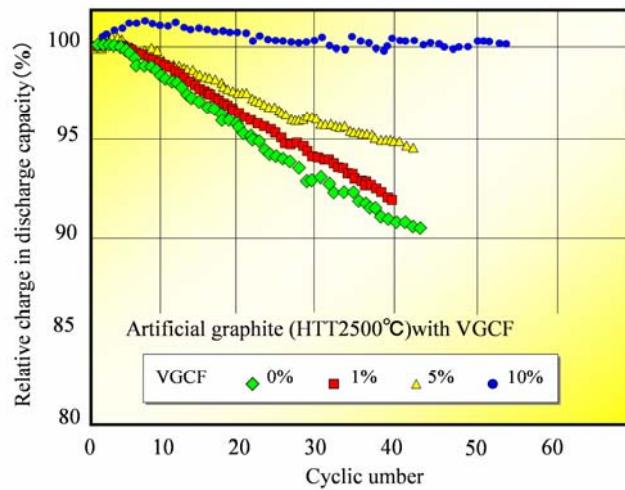
Figure B.14. Dependence of the cyclic charge discharge capacity of an LIB on the weight percent of MWCNTs in the graphite anode (Endo et al. 2001).

MWCNTs containing composites have been molded into submillimeter-sized gears and sporting goods (Figure B.15). No detailed information was provided regarding the wt. % of MWCNTs or the enhanced mechanical properties due to the presence of the MWCNTs.

The scale bar in the left panel corresponds to 200 microns. The Shinshu team recently fabricated a nanocomposite-based microcatheter through-melt extrusion using high-purity carbon nanotubes as filler and nylon as matrix. Homogeneously dispersed carbon nanotubes in nylon lend to enhanced mechanical properties, which are easier to handle, and extremely reduced thrombogenicity or antithrombotic property for the microcatheter (Endo et al. 2005).

Cross-sectional field emission SEM images confirmed that there were no exposed nanotubes both on the inner and outer surface of nanotube-based microcatheter (Figure B.16). The increased elastic modulus (1.5 times), derived from the intrinsic nature of the carbon nanotubes resulted in the recovery to original shape from the bent morphology.
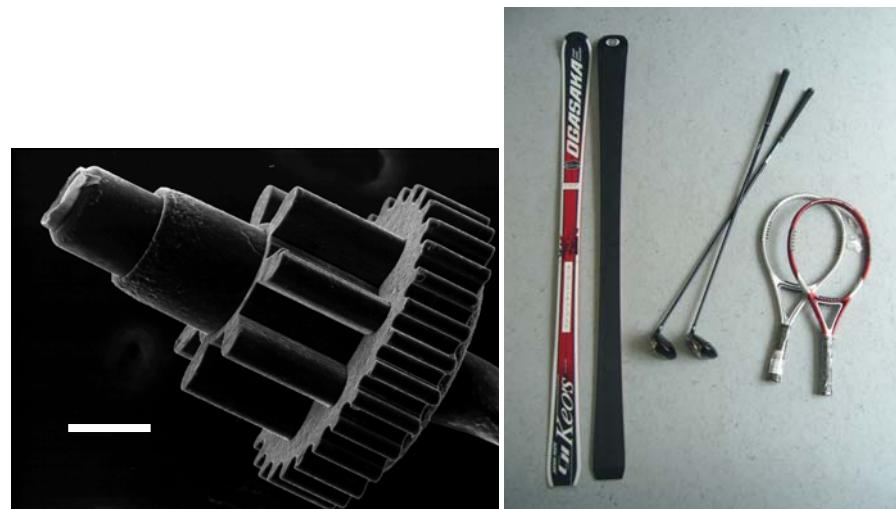
Figure B.15. A variety of MWCNT containing composites prepared by the Shinshu team through collaboration with local industries.
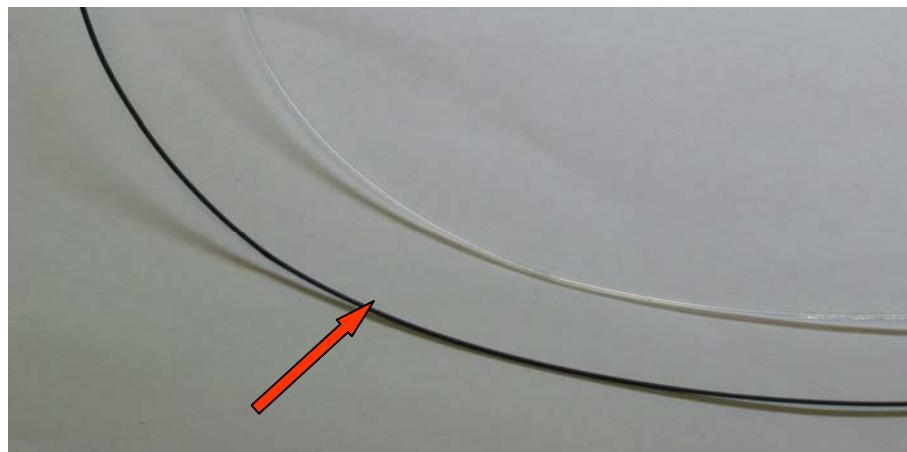
Figure B.16. The image shows a 0.53 mm diameter catheter based on MWCNT/Nylon 12 composite (Endo et al. 2005).

Current research at Shinshu University is focusing on the large-scale production of DWCNTs and nanotubes doped with boron. The advantages of substitutionally doped nanotubes for pristine nanotubes in most applications developed at Shinshu University will be investigated.

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BACKGROUND

Showa Denko (SDK) is a chemical company established in 1939 and headquartered in Tokyo, Japan. With over ten thousand employees, the company has manufacturing activities in areas of chemicals, petrochemicals, ceramics, carbons, aluminum, and electronics materials. The company was initially introduced to us by Dr. Morinobu Endo of Shinshu University. In the area of nanotechnology, SDK has interest in titanium oxide nanoparticles (photocatalysts), zinc oxide nanostructures, fine ceramics, and vapor grown carbon fibers (VGCF[TM]). In addition, the electronics areas are focused on compound semiconductors, LEDs, and hard disks. Before the presentation from representatives of the SDK, Peter Eklund presented an overview of the WTEC mission and goals.

RESEARCH AND DEVELOPMENT ACTIVITIES IN MANUFACTURING

Showa Denko is focused on developing different grades of VGCF[TM] and MWCNTs, specifically for applications in resins (composites) and Li batteries. The company has no activity on single-walled nanotubes. The basic technology for manufacturing of VGCF[TM] (also categorized as MWCNT, especially in the smaller-diameter range) is based on the processes developed by Prof. Endo in the late 1970s and 1980s. Showa Denko has had a long history of collaboration with the Endo group. SDK started the development of VGCF[TM]/MWCNTs in 1982, and had a production capacity of 40 tons/year material at the end of 2000. In 2006, it announced the expansion of this capacity by the end of 2006 to 100 tons/year.

The process for the synthesis of VGCF[TM] is catalytic chemical vapor deposition, based on the technique found decades ago by Dr. Endo. This involves the pyrolisis of hydrocarbons in the presence of catalysts and subsequent graphitization via calcinations at about 3,000°Celsius. Before heat treatment, the fibers have partially disordered structure and contain catalyst particles embedded in them; after calcinations the carbon gets well graphitized, and the catalyst metal particles are almost fully removed. Some basic properties of VGCF[TM]/MWCNTs are shown below (Figure B.17). Different aspect ratios (grades) of these structures are controllably produced by varying the diameter of the structures, and marketed by the company depending on applications.

Fiber diameter	150	nm
Fiber length (average)	10	μ m
Specific gravity	2.19	g/cm^3
Specific surface area	13	m^2/g
Electric Conductivity	0.1	m$\Omega \cdot$cm
Purity	>99.95	Wt%

Figure B.17. VGCF[TM] properties.

APPLICATIONS AND COMMERCIALIZATION

SDK has been manufacturing VGCF^(TM)/MWCNT material for two different applications; one, as additives to electrodes in Li-ion batteries and two, as fillers in composites.

The battery application is commercially available today and is a very large market. The SDK carbon fiber material is added to both anodes (meso-carbon materials) and cathodes (lithium cobalt oxide) in the Li-ion cells. Addition of less than 5% by weight of VGCF^(TM) to the anodes results in good improvements in electrical resistance of the electrode and high rate current performance of the battery (by improving discharge capacity). The cycling performance of the battery is also improved by the addition of the fibers. In the cathode, the addition of fibers allows one to decrease the amount of acetylene black that is normally mixed with the lithium oxide material, improving the electrical resistance and the discharge capacity of the batteries.

The other major application that SDK is involved in with its VGCF^(TM) material is in the area of polymer composites. The basic application being pursued in this space is increasing electrical conductivity (from the use of conducting high aspect ratio fibers) and thermal conductivity. The chart in Figure B.18 shows increase in thermal conductivity demonstrating better performance over traditional carbon fibers and nanotubes.
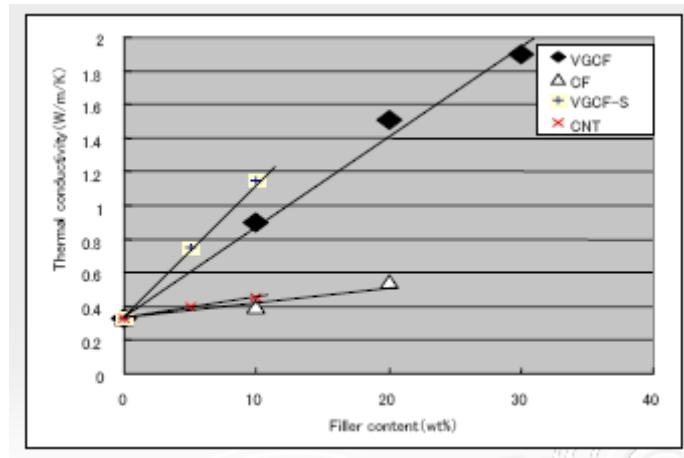
Figure B.18. Comparison of thermal conductivities.

In addition to the applications above, SDK is also interested in developing applications of its VGCF^(TM) material in a variety of electronic (e.g., electrostatic discharge applications with composites), automotive parts (e.g., fuel cells etc.), and other consumer products (e.g., machine tools, display devices, etc.). Although there is no negative data on its materials about safety and health issues by their internal testing, SDK representatives expressed concerned about the safety and health aspects of whole nano material and the company is collaborating with universities to look at this aspect.

SUMMARY

During the WTEC team's visit to SDK, we learned several things about the manufacturing ability, capacity, and commercialization activities of its VGCF^(TM)/MWCNT material. The company anticipates significant growth for its material in the coming years and plans to expand the operation in this area. Our hosts did not show any interest at the present time in getting into single-walled nanotube R&D due to issues related to scalability, cost, and uncertainty regarding health-related issues.

Site: **Sun Nanotech Co., Ltd.**
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                     Nanchang, Jiangxi 330029
                     China
                     www.sunnano.com

Data Visited: September 27, 2006

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BACKGROUND

Sun Nanotech was formed in 1999 and began commercial production of MWCNTs in 2001. As a startup producer of MWCNTs, Sun produces up to five types of MWCNTs for industrial and institutional use. The reference base includes over 400 clients, over 100 of which have been based in the United States.

Sun Nanotech's facility is located in Nanchang, Jiangxi, China. The WTEC team did not see the facility during the meeting with Sun Nanotech management. Photos available from Sun Nanotech's website confirm that the production facility consists of four batch CVD tube furnaces and instrumentation to support quality assurance and product assessment.

Sun Nanotech uses CVD processing (in multiple-tube-type furnaces) (Figure B.19). The facility has a combined annual output of MWCNTs at five tons/year (on a 1-shift/day basis). Maximum instantaneous output is approximately 1 kg/hr (10 kg/day on a 1-shift/day basis). Higher output would be possible with around-the-clock, 24/7 operation. Sun Nanotech uses supported mixed metals (Fe/Ni) for catalysts in the CVD process. The carbon source is acetylene or liquefied petroleum gas (LPG). Sun Nanotech derives different quality products from the different carbon sources and markets tiered products based on the type of carbon source used.

Figure B.19. CVD furnaces.

Sun Nanotech is willing to submit a sample to WTEC for independent analysis if the analytical results are shared with Sun Nanotech. Sun Nanotech is also willing to accept product returns from clients if the client is able to demonstrate shortcomings with the product that has been delivered. The level of occupational safety at Sun Nanotech has not been assessed. Sun Nanotech's facility does include in-house instrumentation for testing of the nanotube purity/quality (Figure B.20).

(a.)   (b.)

(c.)   (d.)
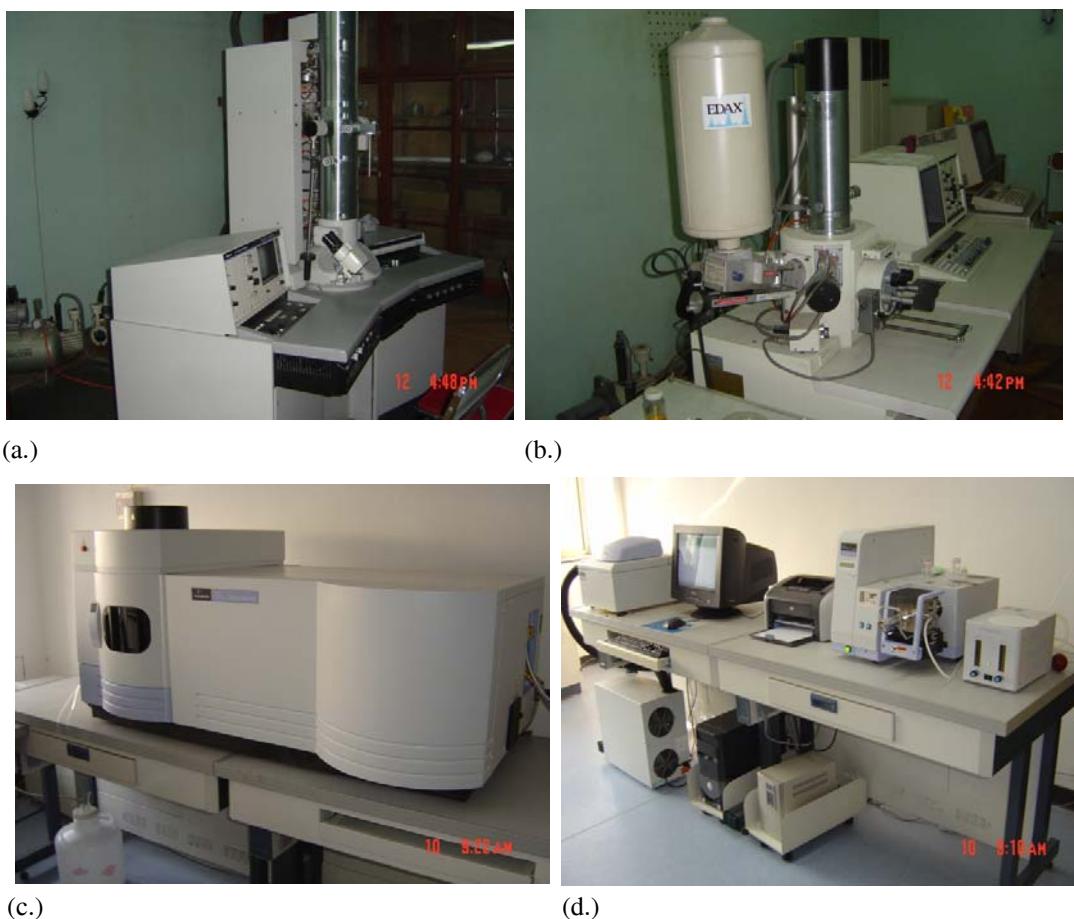
Figure B.20. Testing instruments: (a) TEM (H-600); (b) SEM(S-570); (c) ICP (Optima 5300DV); (d) TG/DTA (Pris Diamond).

RESEARCH AND DEVELOPMENT ACTIVITIES

The WTEC panelists could not assess Sun Nanotech's intellectual property position. Information regarding patents, patent applications, and research is not available from the company website. The company's intellectual property and process know-how are likely considered to be industry trade secrets.

Sun Nanotech is sponsoring R&D in the following areas:

- MWCNTs, SWCNTs, and ANTs
- Carbon nanotube composites
- Supercapacitors
- Hydrogen storage

SUMMARY AND CONCLUSIONS

Sun Nanotech's presentation of its products is summarized on its website and included below as Table B.5. Sun Nanotech anticipates that a 100 ton/year demand will allow it to convert from batch operation to continuous operation. With continuous operation, lower pricing would be possible.

Table B.5. Multiwall Carbon Nanotubes (MWCNTs)

Commodity	MWCNT-L-P	MWCNT-A-P
Purity	>90%	>90%
Residue	<5%	<5%
Diameter	10-30nm	10-30nm
Length	1-10μm	1-10μm
Appearance	Black powder	Black powder
Process	CVD	CVD
Prices	$2/gram	$2/gram
	$1/g (>500g)	$1/g (>500g)
	$400/kg (>5kg)	$400/kg (>5kg)
	$200/kg (>100kg)	$200/kg (>100kg)
Shipment	Express	Express

Carbon sources: L = Liquefied petroleum gas; A = Acetylene

REFERENCES

Sun Nanotech website, www.sunnano.com (accessed on January 17, 2007).

Site:	**Tsinghua University, Tsinghua-Foxconn Nanotechnology Research Center (TFNRC)** **Beijing 100084** **China** **www.tfnrc.tsinghua.edu.cn**
Date Visited:	September 29, 2006
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BACKGROUND

The WTEC team visited the Tsinghua-Foxconn Nanotechnology Research Center (TFNRC), located at Tsinghua University in Beijing. The TFNRC was established in 2003 and is fully funded by Foxconn Corporation, a leading manufacturer of electronics, including personal computers and mobile phones. Foxconn donated the center to Tsinghua University, including $10 to $15 million for a new building (13,000 m^2), and $15 million for state-of-the-art equipment (microfabrication tools, SEM, TEM, e-beam lithography system, etc.). Foxconn also provides approximately $1.5 million annually for operating costs.

The center is a unique model for interdisciplinary, industry-funded, university research. Typically, Foxconn suggests a project area to Tsinghua scientists, and the scientists respond by assembling an interdisciplinary team to address the project. After formulating a project plan, the parties sign a research contract that allocates funding and lab space to the project. Projects typically last three years, and intellectual property (IP) rights are split equally between Tsinghua and Foxconn. The center has six full-time attorneys on site and has filed approximately 700 patent applications (primarily in China, the United States, and Japan) during the past three years.

The TFNRC has a 900 m^2 cleanroom. The cleanroom and characterization facilities are available for shared usage (on a pay-per-use basis) by Tsinghua researchers not associated with the TFNRC.

CNT RESEARCH AND DEVELOPMENT ACTIVITIES

CNT research at the TFNRC is primarily conducted by the group of Prof. Shoushan Fan. The group's core CNT synthesis technology is thermal CVD growth of vertically aligned CNT arrays on silicon substrates (up to full 4" diameter wafers (Figure B.21) (Fan et al. 1999 and Zhang et al. 2006). Prof. Fan's group is creating CNT-polymer films as thermal dissipation interfaces (led by Dr. Changhong Liu) (Huang et al. 2005; Wu et al. 2006; Liu et al. 2006), designing and fabricating nanoelectronic and photonic devices based on 1-dimensional nanomaterials such as CNT and SiNW (led by Dr. Qunqing Li), spinning continuous nanotube yarns from the CNT arrays (led by Dr. Kaili Jiang) (Zhang et al. 2006; Jiang et al. 2002), and studying the field emission performance of CNT arrays and yarns for applications including thermionic emitters and ambient light sources (led by Dr. Liang Liu) (Fan et a;/ 1999; Wei et al. 2005; Liu et al. 2006).

Figure B.21. CNT arrays on 4" silicon wafers, grown from SiO_2-supported Fe in C_2H_2: (left) MWCNT array; (right) SWNT array (top surface of array develops microcracks during growth).

The laboratory has four custom-built, computer-controlled tube furnaces for growth of CNTs and semiconductor nanowires (Figure B.22), as well as a variety of other equipment, including a computer-controlled screen printer, a dedicated e-beam evaporator for deposition of Fe catalyst for CNT growth, many fabrication and testing tools for field emission devices, and additional "manual" furnaces for development of CVD growth processes.

Figure B.22. Computer-controlled tube furnaces for CVD growth of CNTs and nanowires on full 4" wafer substrates. The furnaces are enclosed in a dedicated room, and the gases are stored in a separate room beneath the laboratory.

CNT arrays and bulk (tangled) CNTs are being infiltrated with polymers to create composite films for thermal dissipation, for example, as interface layers for microprocessors. The group has demonstrated that CNTs can significantly increase the thermal conductivity of a polymer, and is actively studying the effect of

CNT surface treatment, length, and contact structure on the bulk and interfacial thermal resistance of these composites.

Flat panel field emission backlights using screen printed CNT cathode have been demonstrated in the laboratory; these prototypes were aimed for LCD backlight and field emission displays (Figure B.23a). CNT emitters were also formed on metal wires to make line-type cathodes and were assembled into field emission luminescent tubes (Figure B.23b) as mercury-free ambient light sources seeking to replace fluorescent lamps. Currently, the power consumption of these prototypes should be reduced significantly for practical applications.
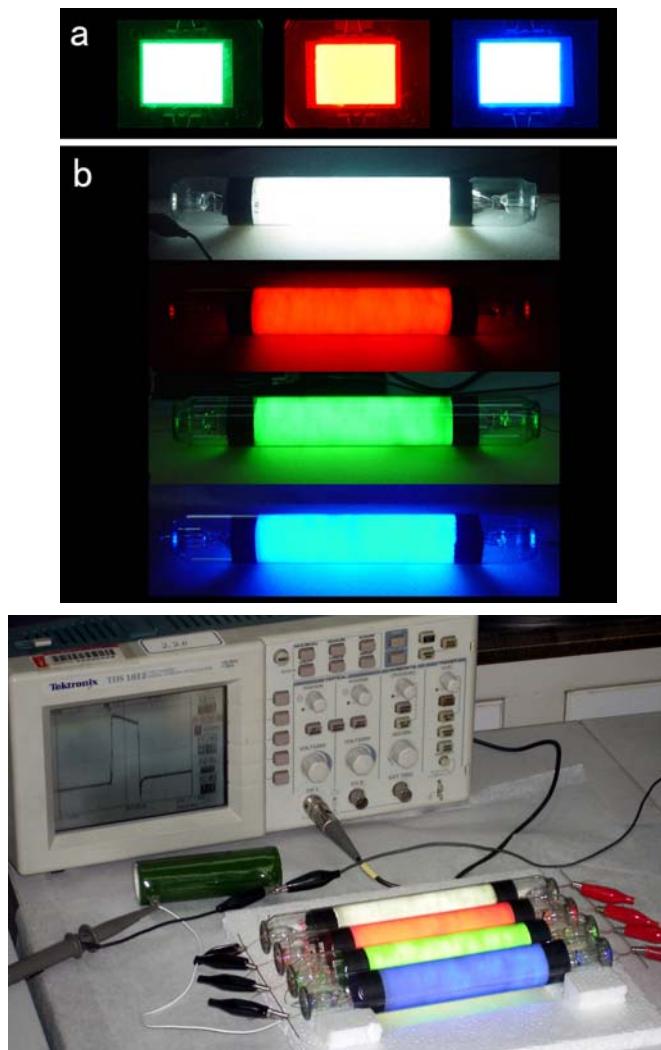

Figure B.23. Prototype field emission light sources using CNT-coated metal wires sealed inside phosphor-lined glass tubes: (a) flat panel backlights; (b) luminescent tubes; (c) alternate view of luminescent tubes.

Continuous CNT yarns are pulled from aligned CNT arrays, where van der Waals forces cause the CNTs to unravel and form a yarn when a section of the film is pulled from the sidewall of the array (Figure B.24). This process was first published by Prof. Fan's group in 2002 (Jiang et al. 2002), and a variation of the process where the yarn is twisted rapidly during pulling was later published by Zhang et al. in 2004. The Tsinghua group has since further developed the process, scaling it to full wafer arrays of "super-aligned" CNTs having a much higher area density, and it has developed a technique to densify the yarn by drawing it through an alcohol droplet. The group has demonstrated a yarn tensile strength of 0.7 GPa, and the yarns exhibit an elastic shape-memory effect when resistively heated. This technique is used to form yarns into coil

springs (Zhang et al. 2006). Field emission from the ends of CNT yarns is currently being studied in detail (Wei et al. 2006). Thermionic CNT yarn emitters are sought as a long-life replacement to LaB_6 filaments, which are commonly used in electron microscopes (Liu et al. 2006).
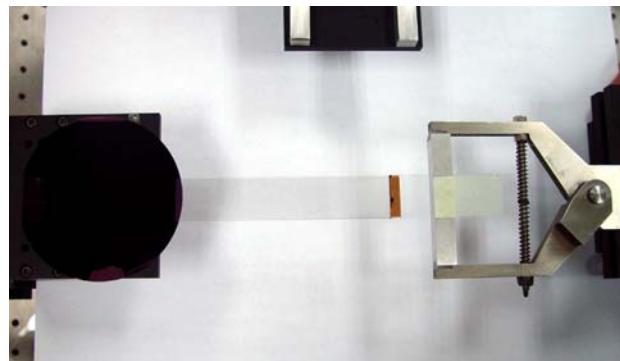

Figure B.24. Spinning CNT films from four-inch superaligned CNT arrays
with a home designed semi-automatic stage.

Finally, there are novel efforts at TFNRC on studying the kinetics of CNT array growth and on modeling of the growth mechanisms. This includes a technique for pulsing the gas flow composition in a tube furnace, which causes a discontinuity in growth and thereby reveals a "ruler" mark on the sidewall of the array (Liu et al. 2005). Further process insight is obtained by optical observation of CNT array growth on a resistively heated substrate.

SUMMARY AND CONCLUSIONS

Based on the large volume of its patent filings and high-profile publications on CNT synthesis and applications, it appears that TFNRC is a successful model for industry-sponsored nanotechnology research, with truly world-class facilities. A large benefit of the arrangement is that funding and space for a new project can be obtained rapidly, contrasting the much longer timeframe for government funding sources.

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Date Visited: September 29, 2006

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BACKGROUND

Within Tsinghua University, the Department of Chemical Engineering's Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology dedicates significant research to the design and function of fluidized bed (FB) reactors, with specific focus in hydrocarbon processing. Historically, the laboratory has been the technology provider for numerous industrial-scale FB reactors within China and at international industrial facilities. The facility also investigates the growth of CNTs using FB technologies.

RESEARCH AND DEVELOPMENT

Within the past six years, the CNT group of the key laboratory has begun to investigate the growth of MWCNTs in FB reactors using a variety (up to 20 types) of metal or mixed metal catalyst types — supported and unsupported. Due to its low cost, the most typical catalyst type used for investigation is iron supported on alumina.

The director of the laboratory and CNT group is Dr. Wei Fei, who has been at Tsinghau University for approximately 16 years. The laboratory maintains a faculty of 15 professors/administrators and keeps 30 Ph.D.-level graduate students and approximately 60 master's-level graduate students. The total count of the laboratory personnel is over 100 persons. The laboratory operates on an annual budget of approximately US$1.2 million, derived mainly from industry-sponsored research. The annual budget typically is distributed 50% to equipment (purchases and/or maintenance) and 50% to operations.

The facility houses a number of FB reactors and testing devices capable of operation and optimization of FB reactors. The testing devices include the following:

- TAP (Temporal Analysis Reactor)
- BET, Infrared spectrum, GC-MS
- High-resolution TEM and high-resolution SEM
- Cold-flow fluid bed reactor (0.42 m*18mm, for FCC process)
- Laser Doppler, PIV, and PDPA for particle and bubble measurements
- 500mm turbulent flow FB reactor
- Automatic heat mode FCC reactor (Riser-Downer) system

Dr. Wei performs most of his MWCNT work using the 500mm turbulent FB reactor. The unit is capable of simultaneous production rates of 15 kg/hr and annual output of 50-100 ton MWCNT/year. The limitation to further output is staffing and operation of the unit on an industrial scale within the confines of the university setting. The laboratory performs funded research, in partnership with many first-rate industrial entities, to evaluate the EM-shielding and ESD properties of composites loaded with MWCNTs grown at the facility. The facility houses a number of experimental devices directly preparing and testing the properties of extruded composites that have been doped with MWCNTs grown at the facility. Dr. Wei's group has done

experiments with loading 0.1%-4% (mass percent) MWCNT in PC, PP, PE, PEO, PET, PET Fiber, and PEEK, etc.

The 500 mm FB reactor is operated at temperatures approaching 700-1200°C. The unit is constructed of metallic (not quartz) materials of construction. Dr. Wei reports little to no loss of purity as a result of the metallic materials of construction. The unit, although capable of longer production runs, is usually run in 30-kg production runs. The unit operates with a 20:1 mass product to mass catalyst efficiency. The as-made MWCNT product from the unit is in the 90–95% purity range. And if necessary, the purity of MWCNTs can be directly increased to 97–98.5% using a special technique.

Operationally, the unit is fed catalyst and carbon source to fluidize the bed. After a batch run is complete, the unit atmosphere is switched to nitrogen to quench the reaction. The product is then transferred from the FB to a hold-down pot; the atmosphere from the hold-down pot is slowly vented through the lab HVAC system. No special entrainment separator or cyclone separator device is employed as carefully controlling the state of MWCNTs. For volume reduction of the product, the group has developed techniques to yield a 5-fold volume reduction. After reduction, the product can be expanded and dispersed with little packing and induced agglomeration.

Dr. Wei believes that MWCNT can be produced on an industrial scale at prices in the range of $50–$80/kg. The group will not move towards industrial production within the university but will rather seek to form a joint venture to produce MWCNT within China once a market and application have been established. Wei anticipates that a production facility of 100 tons/year will be the initial target and will be established within five years.

In addition to MWCNT production, the facility is also investigating the growth of SWCNTs in a FB reactor by control of the catalyst type and size (thickness) (Figure B.25). The group has also investigated post-production purification techniques such as acid washing of the product and high-temperature thermal annealing (above 2000°C).

Figure B.25. Turbulent FB CVD reactor and instrumentation at Tsinghua University.

Figure B.26. 500 mm diameter FB reactor and entrainment separator.

SUMMARY AND CONCLUSIONS

Although Tsinghua University is not currently geared toward industrial production of CNTs, Dr Wei's group expects to establish commercial operation within the coming years. If they are able to establish a quality MWCNT or SWCNT using their production techniques, the group will likely have significant commercial advantage due to the low cost materials of construction and high-volume production rates capable in FB technology.

REFERENCES

Fluidation Lab of Tsinghua University website, www.flotu.org/eng.

www.flotu.org/weifei

Site:	**Yonsei Nanomedical National Core Research Center**
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BACKGROUND

The National Core Research Center for Nanomedical Technology on the campus of Yonsei University was founded in December 2004 by the Korea Science and Engineering Foundation under the Ministry of Science and Technology for the purpose of multidisciplinary research and education in the field of nanomedical science and engineering.

The center is presently comprised of 27 faculty members from the departments of chemistry, microbiology, chemical engineering, neurology, mechanical engineering, pharmacology, and electrical and electronic engineering. The faculty members have their own laboratories and offices in their home departments. The center has a large building that houses space for interdisciplinary projects and shared fabrication facilities. The latter consist of a small cleanroom (~1000 sq. ft) for photolithography, and a broad array of deposition systems (outside the cleanroom) including thermal evaporation, sputtering, and pulsed laser deposition. The WTEC team members were also shown a JEOL 6400 used for imaging and e-beam writing of nanoscale linewidth structures. Animal studies are conducted in another building in the College of Medicine.

The center supports ten master's degree and five Ph.D. candidates per year on full scholarships for students in its interdisciplinary research programs (degrees are awarded within the home departments of the advising faculty).

RESEARCH AND DEVELOPMENT ACTIVITIES

The major research areas of the center consist of the following: ultra-high sensitive nanobiosensors; *in vivo* molecular and cellular imaging using novel, intelligent nanohybrids; target-specific nanomedical therapy; and synthesis and safety evaluation of biocompatible nanomaterials.

The center's fabrication skills at the micron scale looked good, with diverse projects that include analyte detection by microcantilever arrays and nanoparticles for enhanced MRI imaging.

Carbon nanotubes comprise only a small part of the center's present research effort, which is in the nascent stages. The research is aiming toward biosensors, with the central idea being to use nanotubes as electronic channels (in the field effect transistor configuration) that exhibit a modulation of their conductance by the adsorption of biologically relevant analytes. Both individual nanotubes grown by CVD from patterned catalyst islands and nanotube network films deposited by imprint lithography are used. Nanotube growth occurs in a commercial CVD system (Atomate) using methane as the carbon feedstock. Network films are made from bulk purchased nanotubes. Bulk nanotubes are from a variety of suppliers including Carbolex (assessed by our hosts as "good"), CNI (assessed "good"), and Ilgin (assessed as "good, but the purification is tedious").

WTEC Team members were shown some data on the detection of NH_3 by the sensors, which showed decreased resistance on repeated dosing with the vapor, but there was "poor" recovery because the resistive heater planned for this was not yet incorporated into the fabricated devices. There are also plans to link the

nanotubes with ligands to provide specificity toward targeted analytes. We were shown an AFM image of a ligand associated carbon nanotube.

SUMMARY AND CONCLUSIONS

The center follows a good model for fostering interdisciplinary research. The building is new and well equipped with standard microfabrication equipment. Efforts involving carbon nanotubes are in the early stages.

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Yonsei Nanomedical NCRC website, nanomed.yonsei.ac.kr (accessed April 13, 2007).

APPENDIX C. GLOSSARY

AIST	National Institute of Advanced Industrial Science and Technology (Japan)
AFM	Atomic force microscope
CAS	Chinese Academy of Sciences (CAS)
CMOS	Complementary metal–oxide–semiconductor
CNF	Carbon nanofibers
CNI	Carbon Nanotechnologies, Inc.
CNM	Carbon nanotube manufacturing
CNT	Carbon nanotube
CNTFET	CNT field effect transistors
Cu	Copper
CVD	Chemical vapor deposition
CCVD	Catalytic chemical vapor deposition
DARPA	Defense Advanced Research Projects Agency (U.S.)
DMF	Dimethylformamide is the organic compound with the formula $(CH_3)_2NC(O)H$
DWCNT	Double-walled carbon nanotube
EDS	Energy dispersive spectrometry
EMI	Electromagnetic interference
ESD	Electrostatic discharge
EU	European Union
EXAFS	X-ray absorption fine structure
FB	Fluidized bed
Fc	Ferrocene
FED	Field emission devices
FET	Field effect transistors
GM	General Motors (U.S.)
H	Hydrogen
HiPCO	High-pressured CO conversion
HRTEM	High resolution transmission electron microscopy
IP	International patent
ITO	Indium tin oxide
Li	Lithium
LCD	Liquid crystal display
LSI	Large-scale integrated
LPG	Liquefied petroleum gas
MEMS	Micro-Electro-Mechanical Systems
MIT	Massachusetts Institute of Technology (U.S.)

MWCNT	Multi-walled carbon nanotube
NCT	Nano Carbon Technologies (Japan)
NIH	National Institutes of Health (U.S.)
NIBIB	National Institute of Biomedical Imaging and Bioengineering
NIST	National Institutes of Standards and Technology
NNI	National Nanotechnology Initiative
NRAM	Nano random access memory
NRC	National Research Council (Canada)
NSF	National Science Foundation
NSTI	Nano Science and Technology Institute
NT	Nanotechnology
NTP	Shenzhen Nanotechnologies Port (China)
OLED	Organic light-emitting diode
ONR	Office of Naval Research (U.S.)
OSTP	Office of Science and Technology Policy
PC	Polycarbonate, a plastic polymer
PE	Polyethylene, a common plastic polymer
PEEK	Polyetheretherketones (PEEK), also referred to as polyketones, are obtained from aromatic dihalides and bisphenolate salts by nucleophilic substitution
PEO	Polyethylene oxide (PEO)
PEI	Polyethyleneime
PEMFC	Proton exchange membrane fuel cell
PET	Polyethylene terephthalate
PLV	Pulsed laser vaporization
PP	Polypropylene, a plastic polymer
Pt	Platinum
PVP	Polyvinylpyrrolidone
RF	Radio frequency
RIKEN	Institute of Physical and Chemical Research (Japan)
RO	Ring oscillator
RPI	Rensselaer Polytechnic Institute
SEM	Scanning electron microscope
Si	Silicon
SNU	Sun Nanotech Co., Ltd. (China)
SWCNT	Single-walled carbon nanotube
SWeNT	South West NanoTechnologies, Inc.
SWNH	Single-walled carbon nanohorns
TEM	Transmission electron microscope

Ta	Tantalum
Ti	Titanium
TWCNT	Triple-walled carbon nanotubes
VGCF	vapor-grown carbon fibers
VLSI	Very-large-scale integration