Science to Commercialization of Carbon Nanotube Sheet and Yarn

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Abstract: - Improved understanding of the science behind the nanotube synthesis process is driving continuous improvement of nanotube based yarn and sheet materials. Nanotube hybrid materials such as nanotubes and metals are being produced or assembled directly from the reactor which opens up a new arena of possibilities for the design of nanostructured materials. The cost of the materials will also be reduced due to higher yield manufacturing. Improved nanotube/hybrid materials are unique compared with many existing materials. Enticed by the potential commercial value of these materials, more industries are now beginning to supplement or replace their incumbent materials such as copper and composites with nanotube hybrid materials that are lighter, tougher, and carry more electrical current. This paper discusses the science and commercialization of nanotubes/hybrid materials along with a range of emerging applications that will benefit from the improved nanotube materials.

Key-Words: - Carbon nanotube, sheet, yarn, hybrid material, commercialization.

1 Introduction

Science underpins the commercialization of high technology materials such as carbon nanotubes (CNTs). Scientific advances in the nanotube growth process translate into commercial technical advantage [1-8]. Thus the coupling of nanotube science to technology is discussed in this paper. Scientific advances are needed to increase the quality of the nanotubes thus opening more applications. Multiphysics synthesis (MPS) is an area of research that uses multiple physical fields to provide additional parameters to increase control over CNT formation and growth. Another new approach is creating CNT hybrid or multicomponent materials which are assembled directly from the reactor. Assembly of hybrid nanoscale materials opens up a new range of possibilities for the design of nanotube based yarn and sheet materials. The cost of the materials will also be reduced due to higher yield manufacturing. These improved CNT and CNT hybrid materials will have properties that are unique compared with those of many existing materials [1,4]. The potential commercial value of the nanotube materials is prompting more industries to investigate replacing their traditional materials with nanotube hybrid materials that are lighter, tougher, or carry more electrical current. Manufacturing these materials for a range of emerging applications will benefit society broadly. An important factor is that interdisciplinary knowledge and teamwork is usually needed to develop applications of nanotube materials. Often, nanotube materials are not a drop-in replacement for legacy materials. Modification of the nanotubes [9-17] or redesign of components may be needed to fully take advantage of the properties of nanotube materials and this applies to applications like electric motors, medical devices, and composites.

Generally, applications that may benefit from nanotube materials include; (1) electrical applications like power cables, electrical shielding from electromagnetic waves and lightning strike, electronic devices such as field emitters and touch screens, electric motors, energy generation and storage through structural supercapacitors; (2) filtering air and water; (3) multi-functional composites for increased thermal and electrical conduction, structural health monitoring for aircraft and infrastructure applications; and (4) biomedical devices such as biosensors and future implantable devices and millirobots, and 3D printing of CNT based printer filaments. Carbon nanotube materials overall represent a new class of materials that fit in-between light weight and high strength but brittle synthetic fibers, and more conductive but dense metals. The Vision and the Mission of the nanotube community is to replace metals with CNT Hybrid Materials that offer improved performance, efficiency, and sustainable manufacturing. The new materials will provide high value broadly from industrial nanotechnology to consumer products. An overview of nanotube global commercialization activities is presented next followed by a summary of recent developments in the science applications of nanotube materials at the University of Cincinnati Nanoworld Laboratories.

1.1 CNT Commercialization Activities

Globally, the US, China, England, Japan, Korea, Israel, Russia and Belgium are performing synthesis and applications research and commercializing CNT materials. Many companies commercializing nanotube materials were spun out of universities with faculty members from these universities involved in building the companies. Carbon nanotube manufacturing is shaping into three areas; (i) nanotube forests grown on a substrate where the forests can be used directly to be infiltrated with matrix materials, or deposited to form a sheet, or the forests can be dry drawn into sheet or drawn and spun into yarn; (ii) powdered nanotubes grown by several methods including arc discharge and fluidized bed, where the nanotubes can be used as additives to polymers or deposited to form sheet; and (iii) gas phase pyrolysis grown nanotubes that are assembled within the reactor into a sock then sheet and yarn. Work in these three areas is reviewed to help readers to develop a path to successfully commercialize nanotube materials.

(i) Nanotube forests grown on a substrate. These are used for optics, air and water filters, reinforcing laminated composites, fluid absorption, and other uses. A few companies sell these materials (Solarno, General Nano) [18] but the market at present is not large partly due the cost of manufacturing the arrays. Long nanotubes have an advantage of better reinforcement but are more difficult to mix and integrate into materials. Shorter nanotubes have fewer defects and consequently better electrical properties. Substrate grown forests can also be dry drawn into sheet or drawn and spun into yarn. Lintec Company from Japan under license from the University of Texas at Dallas is manufacturing materials in Richardson Tx. using carbon nanotube yarn or sheet drawn from substrate grown nanotubes [18]. Other manufacturing of nanotube sheet in Japan is based on substrate grown arrays. The advantage of substrate grown nanotubes is the high purity of the material. Cost and scalability are limitations. General Nano is a US company manufacturing nanotube sheet material in high volume at low cost. Batch and continuous synthesis processes are used. The sheet has high electrical conductivity and modest strength. Improving properties would increase demand as the price point for manufacturing the nanotube materials is reasonable. CSIRO AU [19] performs nanotube fabric research. In China, Tsinghua and other Universities and State Key Labs supported by the government and industry are investing heavily in nanotechnology including nanotube ribbon drawn from forests for touch screens, nanotube powder for batteries, and other novel applications.

(ii) Powdered nanotubes grown by several methods. These are used as additives or coatings for many applications from tires and composites to electrostatic shields. The powder nanotubes can also be wet extruded into yarn or deposited into buckypaper sheet. Powdered nanotubes is the largest market segment in terms of mass of material produced, but the competition is great. Showa Denko KK stopped production of multi-walled carbon nanotube powder in 2012, Bayer Material Science stopped the production of multi-walled carbon nanotube powder in 2013. The Russian company Ocsial [18] introduced powder single wall carbon nanotubes to the market in 2014 at the low price of \$8/gram. The price is projected to still go lower, perhaps to \$1.5/gram. Nanocyl in Belgium sells multi-wall carbon nanotubes as low as \$0.1/gram. Thus it is very difficult to compete in the market for short powdered nanotubes. China is also manufacturing nanotube powder in large quantities for batteries on buses and for an increasing number of applications. In the US Cheap Tubes and other companies produce carbon nanotube powders. Thomas Swan, Novarials Corporation, US Research Nanomaterials, Inc. and others [18] produce nanotube additives for various applications.

(iii) Gas phase pyrolysis (floating catalyst) grown sheet and yarn. Here nanotubes are formed within the reactor as an aerogel and condensed into sheet and yarn. Nanocomp [18] is a US company manufacturing these nanotube yarn and sheet materials. TorTech Nano Fibers Ltd [18] in Israel is manufacturing nanotube yarn using the floating catalyst method in collaboration with the University of Cambridge. Tsinghua, Shanghai and other Universities and State Key Labs supported by the government and industry are also developing the floating catalyst method. This method produces nanotube sheet and yarn with good strength and electrical properties. Cambridge Nanosystems is commercializing graphene and carbon materials.

Other configurations and uses of nanotubes are also being developed [20-33]. Fei Wei of Tsinghua University in China produces half-meter long one-off nanotubes. This method has not been scaled up. Dr. Wei has explained some of the challenges of growing long nanotubes [34]. Boron nitride nanotubes (BNNT) are gaining interest. A company spun out of NASA, BNNT LLC is mass producing BNNT powder. Boronite is a new company producing BNNT yarn and sheet from a floating catalyst reactor. A large effort in BNNT is also being led by NRC Canada with Tekna Company. Australia has been producing BNNT by ball milling for a long time [18,19]. The Tsinghua–Foxconn Nanotechnology Research Center (TFNRC) in China is located on the campus of Tsinghua University in Beijing and focuses primarily on carbon nanotubes and related nanomaterials [35].

2 Nanotube Science

Nanotube yarn and sheet and their material properties are being improved by different approaches and some are discussed here.

2.1 Multiphysics Synthesis

Multiphysics uses multiple physical fields to provide additional parameters to increase control over CNT formation and growth. This involves improving atomization of the fuel, preheating to condition the inlet gases, and electrostatic and electromagnetic excitation of the gas and plasma mixture. High quality CNT with a Raman G/D ratio of 100 have been produced, Fig-1. TGA is in Fig-2.

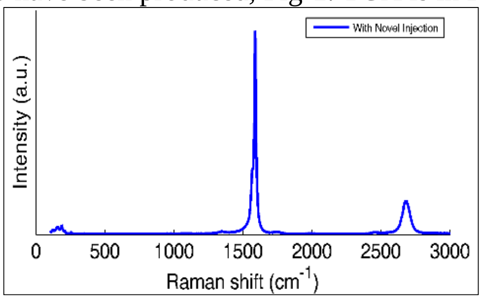

Figure 1. Raman spectrum (with a 785nm excitation laser) of single walled carbon nanotubes produced in the floating catalyst method. G/D is about 100.

A high growth temperature (1400C), short growth time (15 seconds dwell time in a short furnace), and good atomization of the fuel (through a positive displacement injector) are considered the main factors producing the high G/D ratio in this case. The CNT sock exiting the reactor can be rolled into sheet or twisted into yarn, Fig-3. Lightweight CNT-Al sheet is being evaluated and the specific conductivity and specific ampacity compared to Cu.

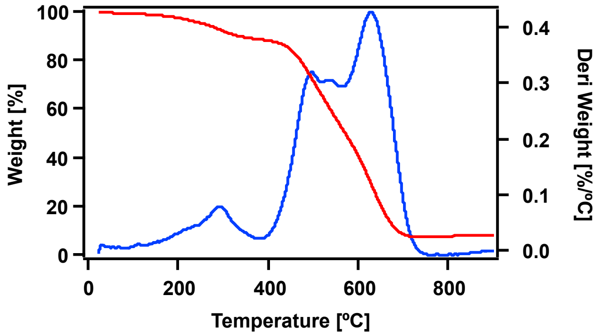

Figure 2. TGA and derivative of single walled CNT.

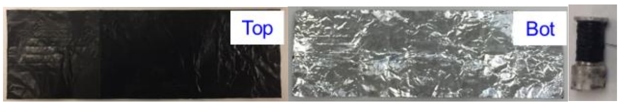

Figure 3. CNT-Al sheet top/bot and CNT yarn produced from the floating catalyst reactor sock.

2.2 Nanotube Hybrid Materials

Presently CNTs are produced in powdered form in large quantities in diameters from 1 nm to 50 nm, with one wall to tens of walls, with lengths from microns to mm, and at a cost from about $100/g for high purity single wall carbon nanotubes (SWCNT) to $10/g for multi-wall CNT (MWCNT), and $400/kg for industrial lower grade MWCNT. CNT powders have applications as additives to polymers and elastomers at generally low loading volume fractions. However, what is needed to really break open large scale commercialization of CNT materials is forming bulk materials from nanoscale materials. There are approaches like (i) dispersion and vacuum filtering to form buckypaper which has limited strength of the paper, and (ii) direct production of a sock and materials from the floating catalyst method, which has yield and cost limitations. Therefore, there is still a need for other methods to form bulk materials from nanoscale materials. The current state of the technology is that the assembly of nanoscale particles to form macro scale materials has mainly been done in the liquid phase [11-13]. Particles are dispersed into fluids or polymers and then dried or cured to form bulk materials [14-16]. Dry drawing or spinning CNT to form sheet and yarn is done from nanotube forests. Synthesis of nanotubes to form a sock which is drawn or twisted to form sheet or thread is done in the floating catalyst method. However, not much attention has been paid to assembling nanoscale materials into macroscale materials in the gas phase. Forming hybrid materials [4] is a new technique to assemble nanoscale materials into bulk materials provided certain conditions including good dispersion of the nanoparticles and having nanoparticles with an aspect ratio that promotes van der Waal attraction.

The overall state of the art of CNT materials is they are light weight, with good thermal/electrical conductivity, moderately strong, and are highly pliable with high ampacity. Limitations are that conductivity needs improvement, and there is considerable difficulty assembling nanoscale materials into macroscale materials. Nanotube hybrid materials is a new Technique in Materials Design and Manufacturing where different nanoscale materials are combined with nanotubes during the nanotube synthesis process. One potential material from this process is CNT wire with improved conductivity, increased yield, lower cost, lightweight, multifunctional, and strong. Other applications are composites, and filters.

Potential applications of nanotube hybrid materials cover different types of materials. Three classes of materials are studied in materials science; metals, polymers, and ceramics. There are also three classes of possible nanotube hybrid materials: (1) Hybrid CNT Metals or CNT-M: M=Cu, Al, Ni; (2) Hybrid CNT Polymers or CNT-P: P=UHMWPE, Buckyball, Single Wall CNT(SWCNT), Elastomer; and (3) Hybrid CNT Ceramics or CNT-C: C=Diamond, Boron Nitride Nanotubes (BNNT), Alum oxide. Nanoparticles are integrated into the CNT synthesis process to form the bulk sheet/yarn materials (eg hybrid materials). Conductive Nanoparticles are introduced into the reactor by a Functional Nano Particle (FNP) Injector. The process is highly tunable and hundreds of material combinations are possible.

2.3.1 van der Waals attraction

Van der Waals (vdw) forces affect the synthesis of nanotube hybrid materials. Vdw force between two parallel CNT is strong [33]. CNT in bundles of 6 or so have reduced attraction to additional CNT otherwise nanotube bundles would become very large. Pressing bundles together may produce a thicker bundle or a thin bundle with stronger vdw forces. Modeling vdw forces in bundles axially and transversely is needed to fully understand how CNT sock and sheet and yarn are formed. Forming bundles can be done by the floating catalyst method where CNT are nucleated from small catalyst particles and the CNT agglomerate into a sock. Another approach may be to disperse CNT in water or a solvent like acetone, dry the water or solvent to allow the CNT to stay relatively dispersed and not agglomerate due to capillary forces. Functionalizing CNT and then assembly [4] may allow a sock to form. Understanding vdw in liquid and air and at high temperature (1400C) is needed to develop a method for forming a sock. The length, purity, quality, straightness of CNT also affect vdw forces. Stretching and annealing CNT may help to increase vdw forces. Vdw forces are needed to make a sock and strong sheet and yarn. There are questions that need to be better answered. Why is very thin CNT sheet strong while thicker sheet is weak? Why is small diameter yarn stronger than larger diameter yarn for yarn with or without twist?

Vdw forces in different gases may affect dispersion of nanoparticles in yarn. Various ways that vdw forces may be affected are considered. Vdw in a plasma (electrically conductive fluid) may affect dispersion of nanotubes. Electrically charging CNT will tend to oppose the vdw forces and may help dispersion. Pressure and injection CNT through a venturi will partly disperse CNT. Higher pressure will better disperse the CNT. CNT bundles that have water or solvent trapped between the CNT may disperse when injected into a hot zone of the furnace as the liquid turns into gas. Van der Waals forces between particles like nanotubes in a gas may not depend on temperature. In the gas phase pyrolysis reaction, Ar gas becomes a weak plasma at temperatures above about 1000C. The plasma is conductive. This plasma might affect the van der walls attraction between nanotubes.

Stopping of the growth of CNT is attributed to many causes including poisoning of the catalyst particles by turning the catalyst into iron carbide or other compounds that do not work well as a catalyst, erosion of the catalyst, encapsulation of the catalyst with a graphene coating that prevents carbon from reaching the catalyst, and other reasons. Another possibility that CNT stop growing is that as they become longer and van der Waals forces increase with the length and the nanotubes start to agglomerate and when two nanotubes stick together that may somehow stop their growth. Electrostatic charging of the fuel or nanotubes helps to repel nanotubes and possibly keep them growing longer. Another approach is shaped reactor tubes that give the nanotubes more room to separate and not agglomerate and stop growing. Forming a sock may be more difficult as the critical density of nanotubes needed to form the sock many not be met. A free body diagram of a surface element of a CNT sock in the gas phase pyrolysis method is used to help understand sock formation, Fig-4.

Bundles of CNT form due to Vdw interaction, and the bundles later assemble into CNT sock under the influence of the flow field. During the CNT synthesis, significant CNTs will deposit on the inner wall of the reactor tube. Once the closed end of the sock forms due to shear induced alignment around the vortex region [17], the CNT sock inflates. The surface of a sock has sufficient entangled CNTs, and this macro entity slides on the reactor wall. This is analogous to CNT powder and buckypaper when they make contact with a substrate, the former attaches easily while the latter can be separated from the substrate.

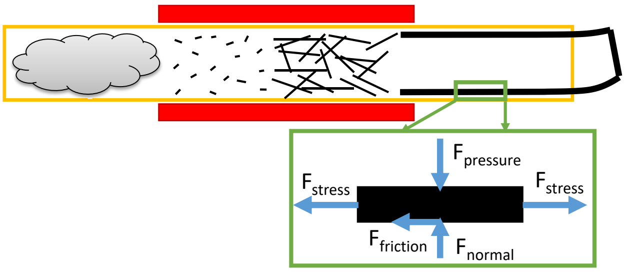

Figure 4. Forces acting on the wall of a CNT sock.

2.3 Manufacturing

The science under investigation in the previous sections is leading to a new area of manufacturing where materials and components are assembled in the gas phase. Understanding and controlling the forces that act on materials at the nanoscale is the principle behind this Manufacturing. Vdw, electrostatic and electromagnetic forces act on materials [33] and these forces can be used to improve the synthesis of nanoscale materials and to assemble nanoscale materials into macroscale materials and components. Vdw forces are important to control the synthesis and extend the growth time of CNTs. Electrostatic forces are important for improving the nucleation of CNTs and for assembling the CNTs into patterned components based on electrostatic assembly or coating. The field of hybrid nanoscale materials is emerging and some concepts were presented as background from which to expand research efforts.

3 Nanotube Commercialization

General areas of potential commercialization of nanotube materials are discussed. Market Revenues for Carbon Nanotubes (2015) were $1.5B with a 22% CAGR thru 2024 [9].

3.1 Electrical Applications

A commercially important target application is to replace Cu electrical wire and shielding with CNT Hybrid wire and sheet. Nanoscale materials such as conductive CNT/Cu hybrid wire and superparamagnetic iron NPs can be manufactured. We expect that the use of these CNT materials to build Square Cage Induction Motors (SQIM) will improve the power density (ratio of output power to weight) of motors. Induction motor performance using iron and Cu materials is limited by hysteresis and eddy current heat losses in the iron core, and stator and rotor winding heat losses. In addition, the conductivity of the copper wires in the stator and rotor coils decreases with increase in temperature. Using CNT wires and a nanomaterials core may decrease the P_{stator} (stator winding heat loss), P_{rotor} (rotor winding heat loss) and P_{fe} (hysteresis & eddy current losses) which approximately add up to 85% of the total motor loss.

Electro-mechanical devices such as electric motors utilize ferromagnetic cores such as iron and steel to provide easier paths for magnetic flux lines. Conductors with lower resistance make the flow of electric current more efficient. Similarly, magnetic cores with lower reluctance make the flow of magnetic flux more efficient. Therefore, we prefer to use a magnetic core with lower reluctance in electromechanical apparatus. The core's low reluctance is directly proportional to the relative permeability of the material used in it. Due to the nonlinear property of permeability, one must use the Flux Intensity vs. Flux Density curves (i.e., B-H curves) to measure the permeability of the cores at different regions of the operating points. Superparamagnetic nano-particles form a composite that has low hysteresis and high saturation magnetization that allows replacement of iron core and rare earth metals in motors. A concept new motor designed based on an induction motors allows operation at high frequencies to take advantage of decreasing electrical impedance of nanotube material. Figure 5 displays the equivalent circuit of an induction motor. Modeling of the motor is the only way to design and optimal motor using nanotube conductors and a soft magnetic core.

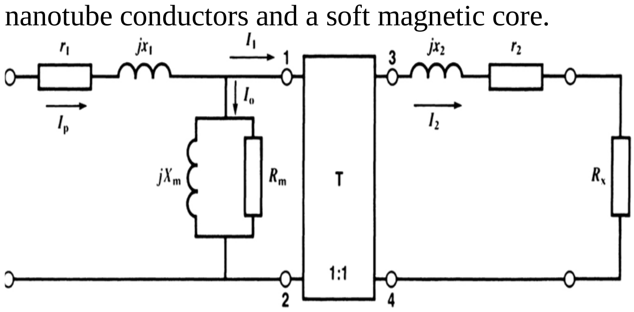

Figure 5. Analysis of induction motor loss ratios, and Per-phase Equivalent Circuit.

The two sources of heat loss in the rotor core called *Hysteresis*, and *Eddy current losses*. Reducing these losses will increase the efficiency of the motors. Electromagnetic cores use laminated cast iron, cast steel, or steel sheet which typically are heavy. We propose using CNT composite materials for the conductor in the rotor core, and soft magnetic material with iron particles as the magnetic core. CNT wire is strong, corrosion resistant, light, and does not have the skin effect in copper at high frequencies. CNT-Cu sheet or wire can form the stator coil windings. The main goal is to eliminate hysteresis and eddy current losses, and to reduce motor weight. Figure 6 displays the rotor of a 3-Phase induction motor manufactured by MotorTec Inc. and a schematic diagram of the proposed CNT induction motor. The rating specification for this MotorTec induction motor is *230 V, Y-connected, 0.25A, 23Watt, 1.2 lb-in @1564 RPM*. CNT conductors and soft magnetic composite materials are being developed to build the squirrel cage Rotor. Then, CNT-Cu wire or sheet will be used for its stator coil windings. To our knowledge, no one has built an electric machine using CNT-Cu sheet and a soft magnetic composite core. Conventional windings in the MotorTec motor are complicated to manufacture using CNT material and SMC material.

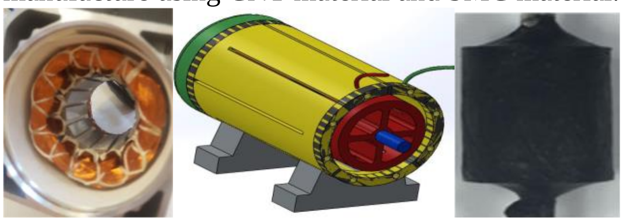

Figure 6. (L-R) The stator of a MotorTec Induction Motor; concept Squirrel Cage Nano Induction Motor; and test rotor built using CNT sheet wrapped on an iron core to replace the standard rotor.

Drop-in replacement of wire and core materials is not the most efficient approach to use nanoscale materials in electric motors. Redesign of the motor such as the Squirrel Cage Nano Induction Motor may be a better approach. The Nano Induction Motor may operate at higher temperature, higher voltage, and higher frequency than conventional motors. Our approach is to: (1) use a rotor consisting of an iron composite core with CNT/CU conductor bars embedded in it. We predict that the soft magnetic composite rotor induction motor will nearly eliminate the eddy current problem as the material has almost no magnetic hysteresis. (2) Electrical conductors will always generate heat equal to I^2R copper loss of the stator coil. CNT-Cu wire 28 AWG wire will be used to wind the stator coils of the MotorTec's induction motor. Another approach is to use CNT Cu sheet for easier manufacturing. Our existing reactor will produce Cu-CNT wire approximately 80 microns in diameter. We plan to use 12 plies of 80 micron Cu-CNT wire twisted together to replace AWG 28 Cu wire. This direct replacement approach enables the use of existing motor design and winding methods. However, in the future redesign of the motor can provide a further reduction in power loss. A motor to take greater advantage of the properties of CNT material may be designed to operate at higher voltage, higher frequency and higher temperature.

The CNT material components of the CNT motor should be compatible with the new induction motor designs, and CNT motors should be easily integrated into the system. Eventually the goal is to design, manufacture and test a nano carbon induction motor which uses CNT, and carbon fiber-composite for all of its components including its shaft and housing. CNT wire is being developed at the University of Cincinnati. High temperature dielectric coatings will also be developed. Materials like aluminum oxide and glass could be used. The CNT induction motor will thus provide: (1) high torque; (2) low eddy current and hysteresis losses; (3) a light weight rotor and stator; and finally (4) manufacturing the motor is sustainable and environmentally friendly.

There will be other applications of CNT hybrid and CNT-metal wires. CNT Hybrid wires are applicable for thin wire applications, small electronic devices, antennas, EMI shielding. Thick wire applications include military vehicles and motors in electric cars. The hybrid materials have greater ampacity but lower conductivity than copper at room temperature and at low frequency. At higher temperature and higher frequencies, the CNT hybrid materials also have lower electrical impedance than Cu. CNT hybrid materials are being formed that are lower density than Cu alone, but have lower conductivity than copper. However, at higher frequency, higher temperature, higher stress levels, for motors with low duty cycles, and for high current density, hybrid wire may exceed the performance of Cu wire.

3.2 Composites Applications

Fiber-reinforced polymer (FRP) composite materials are an attractive alternative to metals as structural components due to their high specific strength and stiffness [1,2,8,20] and are widely used in the aerospace and sports industries where lightweight, stiff materials are paramount. Multifunctional composites that combine the desirable mechanical properties of existing FRPs with other properties (such as conductivity) are of particular interest as even further weight reductions can be gained by combining multiple systems into one smart material.

The two-phase nature of FRP materials (stiff, hard reinforcement phase and softer, binding matrix phase) combined with their laminar structure renders them prone to both de-bonding between the reinforcement and matrix phases, and delamination between the composite layers. As a result, any attempts to add multi-functionality to FRPs must not contribute to early failure by either of these (or by any other) mechanisms. Because of their extremely high conductivity and aspect ratio, CNTs are capable of drastically increasing the conductivity of FRPs at very low volume fractions [21,22] which makes CNT reinforcement of FRPs a promising avenue towards lightweight, multifunctional materials. Indeed, many attempts have been made to incorporate loose CNTs into FRPs; however, because of the high van der Waals attraction between the nanotubes, they tend to form aggregates when mixed into the matrix which increases viscosity and decreases the properties of the composite [23]. An alternative that alleviates the problem of aggregation while still contributing to multi-functionality is to use preformed CNT structures, such as vertically-aligned forests grown from chemical vapor deposition (CVD). The CNTs can be grown either on a separate substrate and then transferred to the composite [24,25] or grown on the actual fibers themselves [26,27]. The materials produced through these methods have shown significant improvements in mechanical and electrical properties; however, they may not be suitable for large scale manufacturing as the planar size of the materials are limited by the size of the CVD reaction chamber.

Because they can be continuously drawn during manufacturing, CNT sheets and yarns offer the opportunity to add multi-functionality to FRP materials in a scalable and easily industrialized manner. Laminated FRP materials that have been reinforced with CNT sheets in the interlaminar regions have shown significant increases in both interlaminar shear strength and in-plane conductivity [27]. The CNT sheets are prepared separately from the other composite components and are simply stacked to achieve the desired thickness and orientation and placed between two lamina. The CNT sheets create a continuous electrical pathway in the plane of the composite, but the through-thickness conductivity remains a challenge as the thin nanotube sheets placed in between the lamina are not able to penetrate through the fiber mats and make large-scale electrical contact in the through-thickness direction.

Stitching with CNT yarn is a potential avenue for increasing the through-thickness conductivity of FRPs while simultaneously increasing the Mode I fracture toughness, G_{Ic}. Attempts to mitigate the delamination of FRPs with stitching have been practiced since the early 1980s. There are notable drawbacks, however, such as the introduction of resin-rich regions around the stitches and the misalignment and warping of the fibers around stitches – both of which can reduce the tensile strength and modulus of the composite [20,28]. Because CNT yarn maintains its strength even under extreme distortion [14,29], the yarn can easily intercalate between the fibers in the FRP without losing its strength. Additionally, because the stiches run vertically through the thickness of the composite, the conductivity in the through-thickness direction could be significantly increased by stitching with CNT yarn. An example of hybrid CNT material is shown in Figure 7 undergoing the G1C fracture toughness test.

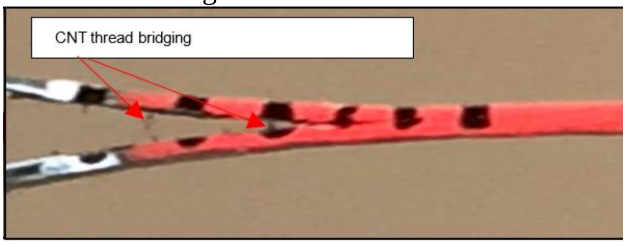

Fig 7. Double cantilever beam test for composites showing a 4-ply CNT thread stitched & CNT sheet patterned glass fabric composite test coupon. Multifunctional composite materials are being developed at the UC Nanoworld Laboratories for high rate manufacturing.

3.3 Filtering Applications

Water and air can be purified using graded CNT sheet which is a nanotube hybrid material. CNT materials have been widely studied as candidate material for water filtration [1,31]. CNT materials can be used as grown or functioned to filter a wide variety of pollutants. However, manufacturing and cost are the factors preventing use of CNT in filters. With the progress in CNT manufacturing such as the catalytic chemical vapor deposition in a fluidized bed, the cost is reducing. Another approach is novel packing of the CNT material for high efficient use. The CNT filtration media with varying porosity in a stratified structure may have improved filtration efficiency as compared uniformly structured filters.

The porosity decreases from top to bottom of the filter, reducing the chance of clogged surface layer. Proper manufacturing and post processing of CNT yarn is the key to make such a stratified filter structure. In filtering, larger particles may plug a fine pore filter, and smaller particles may pass through a coarse pore filter. Thus a graded porosity filter is appropriate for some applications.

Using combinations of CNT/conventional filter may reduce the cost of using CNT in filtration while still achieving superior filtration effectiveness, Fig-8. In the novel nanotube hybrid manufacturing process, conventional filter material can be integrated with CNT, forming hybrid CNT materials. The CNT material is packed together with other filter media particles such as activated carbon and catalytic particles. The hybrid filter media could improve efficiency, capacity and may target a wider spectrum of contaminants. Since the CNT filter is electrically conductive, ionic filtering is also under investigation but is complex.

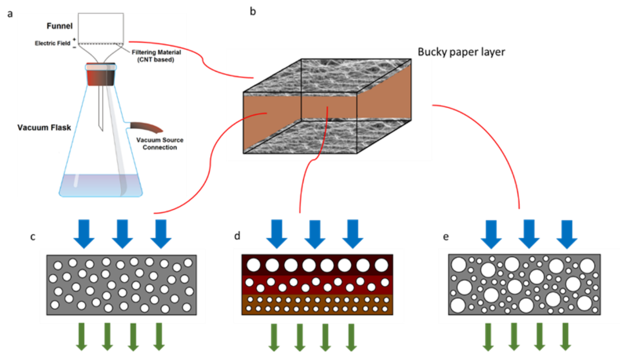

Figure 8. CNT membrane development for water filtering at the University of Cincinnati.

3.4 Biomedical Applications

For the last few decades, biomedical innovations have been focused on making surgeries and complicated medical procedures depend less on the dexterity of the surgeon and more on the cognitive skills of the surgeon. The proliferation of Minimally Invasive Surgery has significantly helped in accomplishing this need of the biomedical industry. However, these Minimally Invasive Surgical devices have hitherto been cumbersome, restrictive to vasculature, and lack the ability to steer flexibly through soft tissue while retaining the ability to actuate. To enable steering, some devices are curved but they are mostly rigid so they can only go one way. A good example of this would be the steerable catheter [36]. The deficiencies of these devices have prevented their use in various parts of the body. To address this need, our group is investigating Precision Internal Medical Devices (PIMDs), by using micro and nano-manufacturing methods and carbon based nano-materials, which are tiny, flexible and less invasive than existing medical devices.

Impedance Sensor. CNT yarns are flexible and conductive. Thus, when covered with an insulated coating, they are a good choice for powering in-vivo devices and sensors. Irreversible electroporation (IRE) is a soft tissue ablation technique using ultra short but strong electric fields to create permanent and hence lethal nanopores in the cell membrane, to disrupt the cellular homeostasis, making this useful for destroying cancerous tissues. As this technique usually [37] brings about a change in the conductivity of the tissue, an impedance sensor would find its application here. A mm sized electroporation device and impedance sensor was prepared by using two CNT yarns so that the device can be maneuvered with a steerable catheter. Electrochemical Impedance Spectroscopy (EIS) is then carried out using the device. Fluoroscopy might be used to image the device in the body to perform sensing or IRE micro-surgery.

Catheter Robot: Conventional catheter tools make it difficult to obtain samples from hard to reach areas of the human as catheters are limited in size. In order to advance in this direction, we have designed a concept catheter robot, Figure 9. A hollow spiral wire tube is guided along vessels using pull-wires. The hollow tube can also be used for suction or to deliver fluids or air (when used in the lungs). In further designs, a flexible drive shaft powered by an electric motor in a larger section of the robot can be used. A blade at the tip of the actuator can be used to cut tissue and the vacuum draws the tissue through the tube.

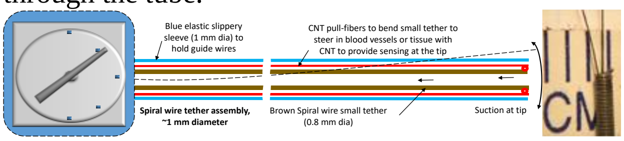

Figure 9. (L-R) Concept catheter robot for sampling, fluid delivery. CNT wire provides sensing, power.; Spiral sheath 0.9 mm OD, two CNT wires inside.

PIMDs use flexible CNT yarn for power or to cross the skin. The long term innovation of this research is the development of minimally invasive directional millirobots to enable the detection (sensing and sampling) and treatment (tissue ablation, drug delivery, structural support) of lung cancer at early stages. The millirobots will have different functional modules that perform different tasks. This concept millirobot that can reach distal airways that are currently inaccessible during interventional bronchoscopy. The millirobot tip is 1 mm in diameter. A spiral tether will be used to guide the robot through the complex curvature of air passages. The tiny robot can turn and remove tissue at a tumor or provide therapy through drug delivery.

3.5 3-D Printing Applications
Fused filament fabrication is a 3D printing technology that translates plastic filaments into three-dimensional parts. Nanotube powder has been used in 3D printing filament but the properties improvement is modest since the volume fraction of the CNT is small, and the CNT do not bridge the electrical conductivity or load across the produced part. Here, CNT yarn is integrated into filament. Presently, there is an unmet demand to translate this technology into a full-scale manufacturing process. With advancements in hardware components and build preparation software, the main component that has been holding back progress in 3D Printing industry is the filament material. The majority of the plastic filaments in the market lack performance characteristics such as strength, durability and electrical properties. Reinforcing the standard plastic filaments with a strong multifunctional nanomaterial like CNT will drastically improve the capabilities of 3D Printed parts. In this research, several techniques were tested to implement custom fibers into standard plastic filaments. An innovative filament production system was developed to produce CNT yarn reinforced 3D Printing filaments. Figure 10 shows sample material produced.

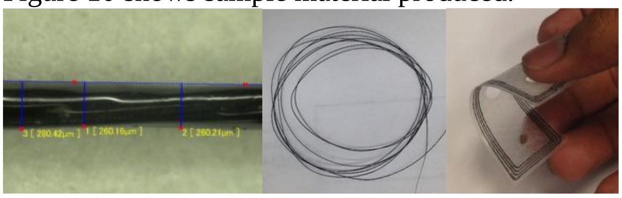

Figure 10. (L-R) CNT fiber composite filament; Spool of CNT filament – about 6m; manually flexing the printed part [32].

4 Conclusions
The main conclusions that can be drawn from the work in progress described in this paper are that the various science techniques and commercialization efforts underway are making progress toward producing a improved nanotube and hybrid materials that will replace existing fiber materials across broad areas of engineering.

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