Ultra-High Conductivity Umbilicals: A Paradigm Change in Conductors Using Carbon Nanotubes

Study sponsored by:
Research Partnership to Secure Energy for America (RPSEA)

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March 2, 2010

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1.0 EXECUTIVE SUMMARY

As offshore developments move into deeper water and step-out distances become longer, there is an increasing need to improve subsea power umbilicals. As water depths increase, a point is reached where hang-off weights become large and conventional copper (Cu) wire cannot support its own weight. Thus alternative conductors are needed. Since individual carbon nanotubes are considered to have conductivity 10 times better than the traditional Cu used in umbilicals today and are ~9 times lighter, they are an ideal candidate to replace copper and perhaps other metal conductors as well (e.g. aluminum). One way to produce a nanotube conducting wire is to incorporate nanotubes into a polymer that enables the electrical transfer of power through the nanotube conduits. The nanotubes serve as the conductor in a polymer matrix that will be neutrally buoyant.

The overall objective of this year long study was to design, build, and test an engineering prototype of a working ultra-high conductivity 'wire', also referred to as a polymeric conductor. In its most ideal form, the polymeric conductor would be at least one foot long - and operating at room temperature, be demonstrated to carry at least 500 amps, at one half the diameter of a pure copper conductor carrying the same current at the same voltage. This prototype, in later stages, could be incorporated into an umbilical. Such an umbilical, termed polymer nanotube umbilical (PNU), will be expected to exceed 100 miles in length and be called upon to deliver up to 10 MW at up to 36 kV with operating envelopes ranging from ~30 – 250°F and pressures from 0 – 4500 psi.

Primary deliverables of the project were met; however the most ideal form of the conductor was not achieved. Work completed during the project year dictates a continuation of effort to achieve the ultimate goal of a PNU in an offshore application. Key findings of the project include:

- Produced polymeric conductors with nanotube concentrations up to 90 wt%; however, the primary focus of the program was directed toward low concentration samples.
- Reached a minimum resistivity (inverse of conductivity) value of $2x10^{-2}$ $\Omega \cdot$cm in the melt state.
- Conductor carried a maximum voltage of 40V (the limit has not been evaluated).
- Conductor carried a maximum current of 16 A (not fully optimized).
- Identified several new steps for lowering resistivity.

2.0 INDUSTRY NEED

As offshore developments move both into deeper water (excess of 10,000') and longer step-out distances (excess of 30 miles) there is an increasing need to improve subsea power umbilicals. Umbilicals must withstand substantial installation (laying) and service loads and load combinations as well as perform their functions for an extended design life (typically 20 years). As water depths increase, conventional copper (Cu) wire cannot support its own weight so new conductors are needed. An increasingly important use of umbilicals is the transmission of electrical power to electrical devices on the seabed. In offshore developments for oil and gas, there is a need to deliver significant amounts of power to subsea installations, particularly for artificial lift systems incorporating electrical motors.

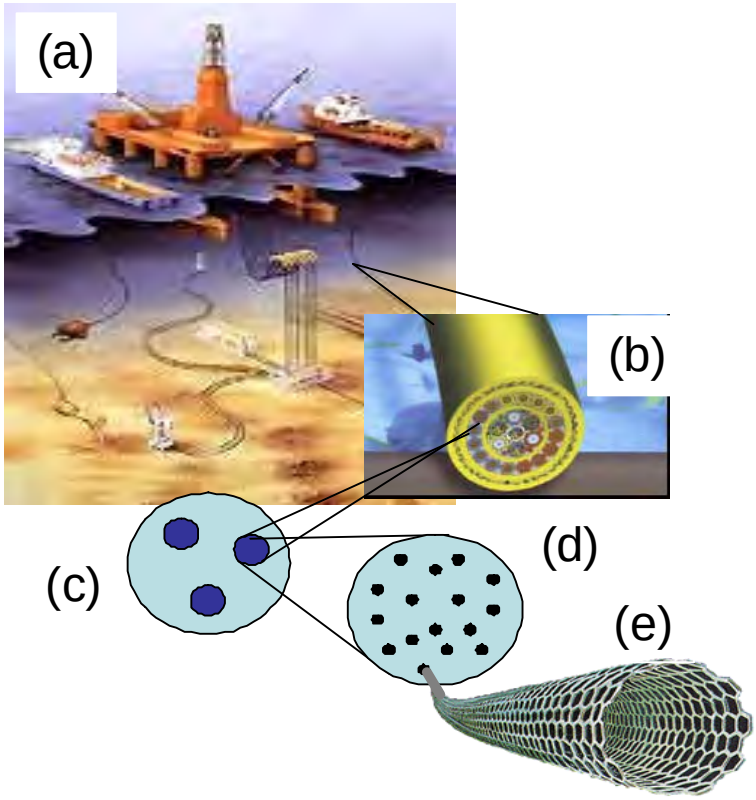


Figure 1 - Projected schematic of a Polymer Nanotube Umbilical (PNU) wire used in an umbilical system for oil and gas production [1]

Figure 1 above shows a projected view of umbilicals used in oil and gas production from an offshore oil and gas platform. Figure 1(a) shows the umbilicals spanning from the platform to the seafloor. Figure 1(b) shows the cross-section of a multipurpose umbilical. The umbilical can include hydraulic lines, communication electrical wiring, and power lines

for pump operation. Figure 1(c) shows the cross-section of an electrical umbilical (shown as wired for a three phase conductor). Figure 1(d) shows the nanotube based wire, while Figure 1(e) shows the cross-section of the nanotube filled polymer wire. The new Polymer Nanotube Umbilical (PNU) proposed in this program is a single-walled carbon nanotube filled polymer wire. This paradigm change in conducting wire is enabled by the high conductivity of the nanotubes and the understanding developed in processing and manufacturing nanotube filled polymers. Nanotubes are considered to have conductivity 10 times better than Cu [2, 3]. Nanotubes offer lightweight conductors (better than silver) and do not require the cooling systems of superconducting wires. The focus on producing a nanotube conducting wire is to assemble nanotubes into a polymer that enables the electrical transfer of power through the nanotube conduits. Nanotubes have very high current density and can therefore become a conductor for high power transfer when well dispersed in a polymer. The polymer filler serves as a binder for the nanotubes and can enable a high strength wire as further properties are developed.

3.0 SCOPE OF WORK

The overall objective of this study is to design, build, and test an engineering prototype of a working ultra-high conductivity 'wire' (see Figure 1(d)), also referred to as a polymeric conductor, that could in later stages be incorporated into an umbilical exceeding 100 miles in length and called upon to deliver up to 10 MW at up to 36 kV with operating envelopes ranging from ~30 – 250°F and pressures from 0 – 4500 psi.

The three main deliverables for the project were:

- Deliver an actual piece of polymeric conductor. The conductor shall be at least one foot long, and operating at room temperature, be demonstrated to carry at least 500 amps and be one half the diameter of a pure copper conductor carrying the same current and voltage.
- Conduct a workshop in Houston, Texas to present and discuss results.
- Deliver a final report that documents the results of the demonstration.
    - An explanation and discussion of how to potentially manufacture the conductors for industrial use.
    - Preliminary economics of the long term costs.
    - Identification of the remaining technical and engineering hurdles.

The engineering prototype is a polymeric conductive 'wire' consisting of nanotubes embedded in a polymer matrix. Tests and analyses were performed, from both a technical and a commercial perspective, to determine and qualify the strengths, weaknesses, and opportunities of further maturing the technology.

Research was performed to advance conduction of the nanotubes themselves to enable future conductors. The steps taken to deliver this engineering prototype wire were as follows:

- Implemented single-walled carbon nanotube (SWNT) technology for achieving conduction.
- Attempted to use metallic SWNTs (m-SWNTs) and were unable to find a source that could provide sufficient quantities.
- Studied nanotube to nanotube (NT-NT) connection to promote low contact resistance.
- Processed NT-NT electrical connections to lower contact resistance.

- Implemented the processing of nanotubes into a polymer binder to form a conducting polymer.
- Used electric fields to promote nanotube alignment.
- Conducted materials characterization at the nano and micro scale levels.
- Conducted small scale electrical conduction tests to evaluate conductivity and NT-NT connectedness.

The level of electrical conduction achieved in the polymeric conductor was accomplished by:

- Use of nanotubes.
- Thermal management of the nanotubes.
- Developing conduction beyond that needed for ESD, EMI.

To produce a polymeric conductor, a number of technological advances were attempted, including:

- Nanotube purification by selected approaches (scaled for producing amounts needed for this program).
- Mixing the SWNTs in polymers and achieving dispersion.
- Use of alignment from extrusion and electric fields.

4.0 PROJECT ORGANIZATION

The Ultra-High Conductivity Umbilicals study was completed in a one year time frame relying on the knowledge and skills of the project team. The technical portion of the project was conducted by Rice University and NanoRidge Materials, Inc. NanoRidge Materials also served as the project manager. Technip, USA and DUCO provided guidance support relating to umbilical use and development. Chevron provided financial assistance. Some personnel of the key contributing organizations are listed below:

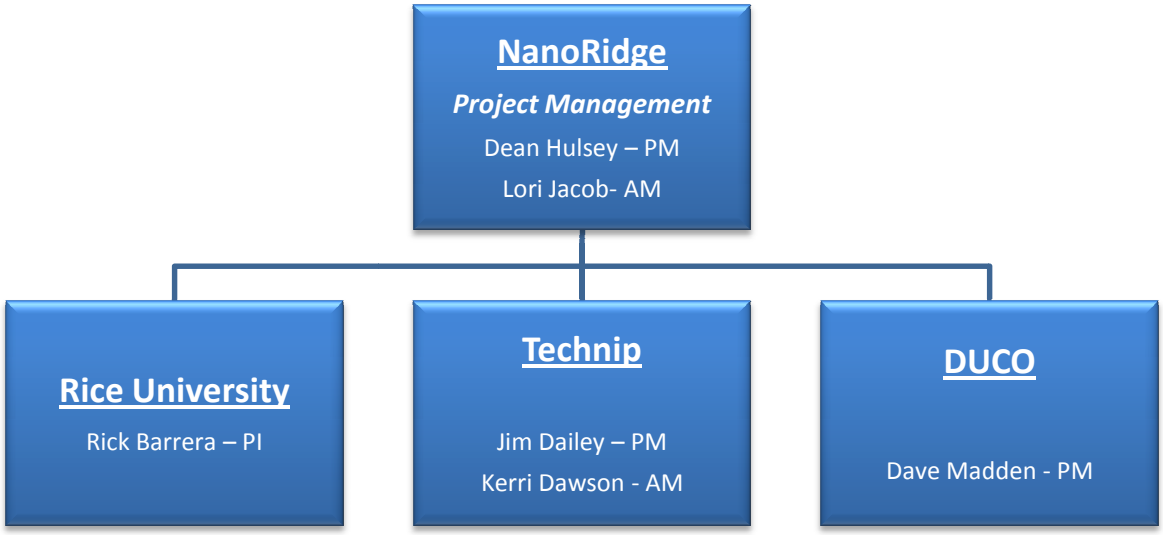


Figure 2 Organizational chart

5.0 KEY COMPONENTS OF THE COMPOSITE

5.1 Polymers

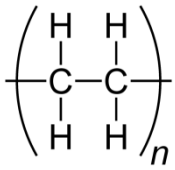
Two polymers were suggested for use in the statement of work: polyethylene and polyamide. These polymers were originally chosen based on recommendations from the umbilical manufacturers. Current umbilicals are composed of a flexible package typically comprised of a thermoplastic extruded layer surrounding a bundle of functional components. These are then assembled together in a compact structure.

The project team selected polyethylene, of various densities, as the chief experimental polymer. This selection was due to availability, processability, and variability allowed in the three densities used. Polystyrene and Dymax (UV curable polyurethane) were also used for certain experiments when necessary. General descriptions of these polymers are given below. Polyamide was not used due to time constraints of testing multiple similar polymers. The choice of polymers did not appear to have any effect on the level of conductivity obtained in the experiments.

5.1.1 Polyethylene (PE)

Polyethylene (PE) is a widely used plastic. It is a polymer of ethylene, CH2=CH2, having the formula (−CH2−CH2−)*n*. Polyethylene is resistant to water, acids, alkalis, and most solvents.

PE is the most widely used plastic, with an annual production of approximately 80 million metric tons.



PE is divided into various density grades. The following three types were used for the purposes of this investigation.

<u>High Density PE (HDPE)</u> is defined by a density of greater or equal to 0.941 g/cm^3. HDPE has a low degree of branching and has strong intermolecular forces and tensile strength.

<u>Medium Density PE (MDPE)</u> is defined by a density range of 0.926–0.940 g/cm^3. MDPE has good shock and drop resistance properties. It also is less notch sensitive than HDPE and stress cracking resistance is better than HDPE.

Low Density PE (LDPE) is defined by a density range of 0.910–0.940 g/cm^3. LDPE has a high degree of short and long chain branching, which means that the chains do not pack into the crystal structure as well. This results in a lower tensile strength and increased ductility. The high degree of branching with long chains gives molten LDPE unique and desirable flow properties.

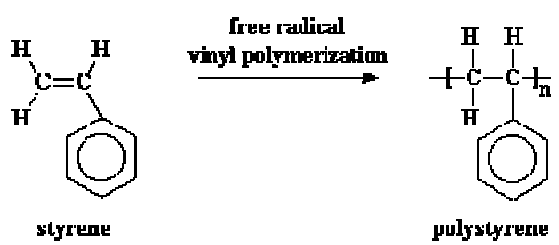
Depending on the crystallinity and molecular weight, a melting point and glass transition may or may not be observable. The temperature at which these occur varies widely with the type of polyethylene. For common commercial grades of MDPE and HDPE the melting point is typically in the range 120 to 130 °C (250 to 265 °F). The melting point for average, commercial, LDPE is typically 105 to 115 °C (220 to 240 °F).

Most LDPE, MDPE and HDPE grades have excellent chemical resistance and do not dissolve at room temperature because of their crystallinity. Polyethylene (other than cross-linked polyethylene) usually can be dissolved at elevated temperatures in aromatic hydrocarbons such as toluene or xylene, or in chlorinated solvents such as trichloroethane or trichlorobenzene.

5.1.2 Polystyrene (PS)

Polystyrene (PS) is a widely used plastic. It is a colorless, transparent thermoplastic that softens slightly above 100°C (212°F) and becomes a viscous liquid at around 185°C (365°F). It is resistant to acids, alkalis, oils, and alcohols.

PS is a vinyl polymer. Structurally, it is a long hydrocarbon chain, with a phenyl group attached to every other carbon atom.



Polystyrene was mainly used for annealing experiments in this project to replicate findings in prior research [4].

5.1.3 Dymax

The Dymax material used in the project was **Ultra Light-Weld® 3091,** an adhesive that is designed for rapid bonding of poly vinyl chloride, nylon, polycarbonate, polyurethane, styrene, and other plastic substrates. Dymax materials are solvent free and cure upon exposure to light. This product was chosen for experimentation due to the relatively low viscosity prior to curing, allowing for manipulation of the nanotubes toward alignment.

Table 1 Dymax properties

Viscosity (nominal)	Shore Hardness	Elongation at Break
300 cP	D55	200%

5.2 Nanotubes

Carbon nanotubes (CNTs) are crystalline, lattice graphene sheets rolled into tube-shaped structures, closed on each end and measuring 1 to 3 nm in diameter. CNTs can measure up to 10,000 nm long and can exhibit unusually high aspect (length-to-diameter) ratios (as great as 10,000:1) that are a key factor in their performance. Single-walled carbon nanotubes (SWNTs) are comprised of a single tube with one wall. Multiwalled carbon nanotubes (MWNTs) comprise two or more tubes of progressively larger diameter — tubes within tubes. Because of this, MWNTs tend to be slightly larger in diameter (8 to 10 nm). SWNTs are more electrically conductive than MWNTs, but also more expensive and difficult to manufacture.

Nanotubes are the material of choice to promote electrical conduction in the polymers. Of the dozens of known nanotube types, one third are metallic; the rest are direct band-gap semiconductors (depending on the processing mode).

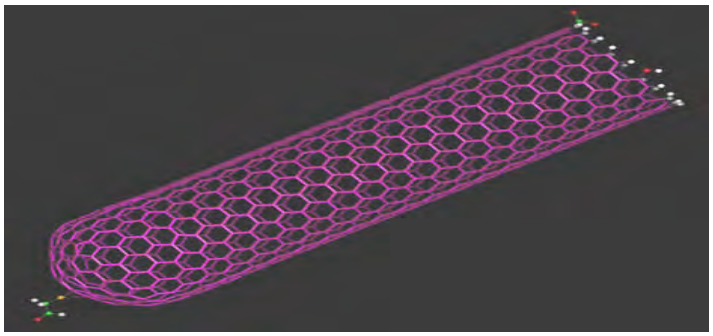


Figure 3 Depiction of a carbon nanotube (Rice University)

The metallic nanotubes, especially the 'armchair' nanotubes, have been shown to conduct electricity at least as well as copper, and perhaps ten times better. SWNTs typically have the following properties:

- Dimensions: 1nm (dia.), 0.3 – 100 mm (length)
- Density: 0.89g/cm^3
- Tensile strength ~50GPa
- Tensile Modulus ~1TPa
- Elongation to failure ~5%

- Electrical Conductivity ~1800-2000 $ohms^{-1}$
- Thermal conductivity - low in transverse direction and high in axial direction (~2500 W/m•K)
- Bound to each other by van der Waals forces
- Can be chemically functionalized

Optimizing the concentration of the SWNTs would ensure cost control. The project team did use SWNTs for many experiments, with MWNTs being utilized when large quantities were required. The metallic SWNTs are not yet available for scaled use. The nanotubes used in this project are listed in Table 2:

Table 2 Nanotubes used in project

Source	Nanotube Type	Summary of Evaluation
Rice University (HiPco)	SWNT	Low amorphous carbon, high catalyst content, very good nanotube sidewall integrity.
Southwest NanoTechnologies (SWeNT)	SWNT	As-received material contains very little metal catalyst or amorphous carbon impurities. [commercial grade (CG)]
Bayer	MWNT	Good quality MWNTs suitable for testing applications, but not a good choice for most conductive applications.

6.0 MANUFACTURING THE CONDUCTOR

In this project, nanotubes are mixed into a polymer matrix. Theoretical prediction indicates that the network of slightly misaligned, highly dispersed, and well connected nanotubes should maximize the conductivity, especially if the nanotubes have the same chirality and are all metallic. In real practice, four issues are involved: dispersion, alignment, connection, and chirality.

Within this section, methods of producing a polymeric conductor wire or sample are described in detail. Differing methods and combinations were researched and used to create a composite wire or small amount of sample for testing in order to increase overall conductivity of the nanotube polymer. Despite the many combinations that were used, the level of improvement for each method ranged from 20 – 70% conductivity improvement compared to the base nanotube polymer. In further research, it is expected that each of these processes continue to be studied and improved upon and ultimately used in combination to create a more conductive sample.

6.1 General Procedure Used to Produce Composite Wire

Rice University developed an incipient wetting procedure for dispersing nanotubes within a polymer matrix. The incipient wetting includes two steps: mixing in the solution and removal of the solvent. High density polyethylene (HDPE) and medium density polyethylene (MDPE) were chosen as the polymers. The procedure for the HDPE/CNTs system involved mixing of the polymer and nanotubes in the solvent, removal of the solvent in a drying step, shear and mechanical mixing, followed by extrusion. Figure 4 shows the schematic of the fabrication process. When using the MDPE, a variation of the previous procedure was used that produced a porous structure on the surface of the MDPE powder. The nanotubes in this system are better dispersed than in the CNTs/HDPE system since the porous structure has a larger contact area between the CNTs and the polymer matrix.

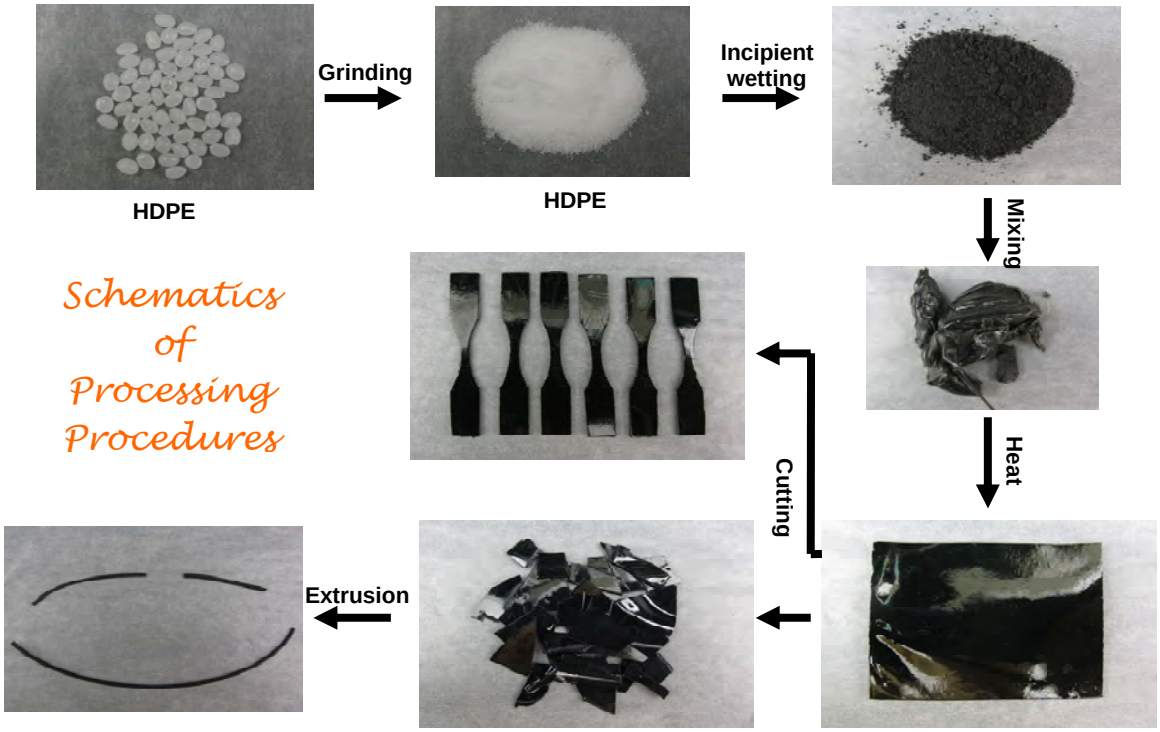


Figure 4 General composite wire processing procedure schematic

Four manufacturing techniques were employed in the production of the composite wires. Initially, composite wires were produced using an injection molding machine, using only 3 grams of starting materials. Injection speed can be adjusted by controlling the injection pressure and the flow rate controlling the degree of nanotube alignment. Other equipment used included a miniextruder, a Haake extruder, and a Lab Scientific extruder. The minimum material requirements for the miniextruder, Haake extruder, and Lab Scientific extruder are 10 grams, 100 grams and 200 grams, respectively. The three extruders each have temperature control and torque control functions.

6.2 Nanotube Purification

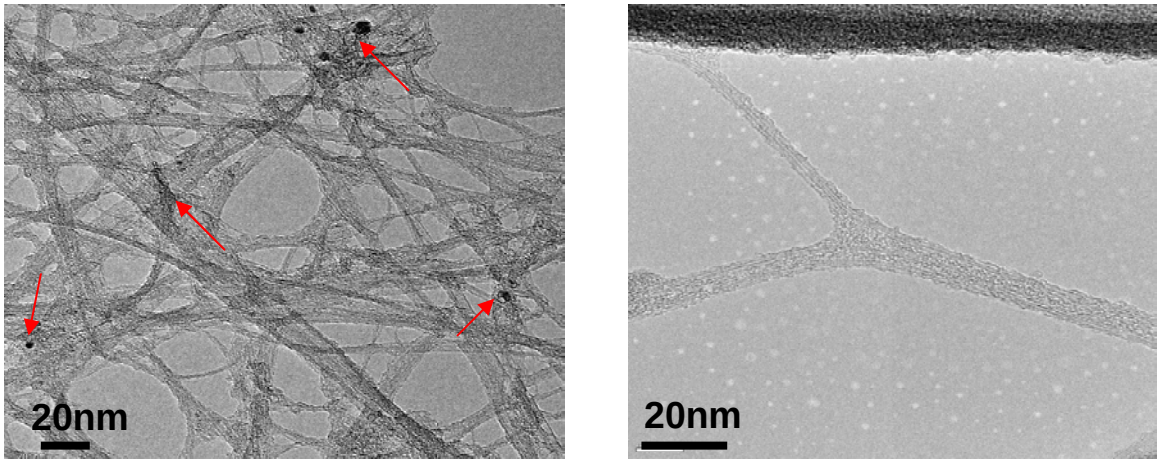
Nanotubes from various suppliers contain different levels of impurities (amorphous carbon and residual catalyst) that are dependent on the manufacturing conditions. In this project, three types of nanotubes were used, HiPco nanotubes, SWeNT CG nanotubes, and Bayer multi-walled nanotubes. Samples were characterized by thermogravimetric analysis (TGA) to measure the levels of impurities. TGA reveals that the initial impurities of raw HiPco nanotubes are 35 weight percent (wt%) iron, with SWeNT and Bayer nanotubes having residual catalyst content below 5%. Prior to utilization, the HiPco nanotubes were purified using an in-house purification method. This method was necessary because other commonly used purification methods damage the nanotubes, resulting in decreased

conductivity. The impurity concentration of HiPco nanotubes decreases from 35 wt% to less than 5 wt% after purification. Raman analysis was also performed to assess nanotube sidewall damage resulting from the purification. It was revealed that nanotube integrity was preserved.

6.3 Dispersion Methods

In order to effectively use the good electrical properties of carbon nanotubes, efficient dispersion of nanotubes and a network formation for electron flow in the composite is essential. To achieve this, an experiment based on the Winey method was used [5]. CG-SWNTs (0.2 mg/ml) were sonicated in dimethylformamide (DMF), n-methylpyrrolidone (NMP), and dichlorobenzene (DCB) for 3 hours using an ultrasonic probe sonicator. Dichlorobenzene was used for processing the CG-SWNTs/MDPE composites, since PE dissolves in dichlorobenzene and the experimental process, hot coagulation, requires a solvent which will disperse the SWNTs and also dissolve the PE.

To remove the larger agglomerates, a decanting process was employed. The samples were centrifuged at different G forces for varying lengths of time. To separate out the catalyst particles, amorphous carbon, and larger agglomerates, the CG-SWNTs in DCB samples needed to be centrifuged at 85000 Gs for 15 minutes. Figure 5 shows the TEM images of the CG-SWNTs before and after decanting. The red arrows indicating dark spots in the TEM image of the sample before decanting shows the presence of left over catalyst particles. It can also be seen that the nanotubes are heavily agglomerated before decanting as compared to after the decanting process. These images are representative of the entire sample since an average of 10 samples were analyzed using TEM.



Before Decanting After Decanting

Figure 5 TEM image of the CG-SWNT/DCB suspensions before and after decanting

A weight analysis on the pellet showed that 30% of the original sample precipitated out of the solution. Clean non-agglomerated CNTs and smaller diameter bundles of CNTs were obtained.

6.4 Extrusion and Alignment Methods

In polymeric conductor manufacturing, nanotube alignment is critical for improving the conductivity of the composites. Shear force and electrical field application are two methods used to align nanotubes. The methods are sometimes used in tandem. A twin screw extruder was employed by NanoRidge to deliver shear forces to the sample. Extrusion speed and pressure could be adjusted as part of optimization of the sample. An electrical field, described further in Section 6.6.2 as a post processing technique, was applied with shear flow direction. Nanotubes are polarized and the nanotubes rotate to align in the direction of the electrical field.

The nanotubes in the composite are wrapped by polymer. The polymer acts as an insulating layer between nanotubes and breaks the conducting paths within the composites. In order to enhance the conductivity, the insulating wrapped polymer layer must be opened up. An attempt was made to connect the nanotubes using an electric field. This provides local heating that can melt the polymer, enhancing the direct contact of the nanotubes.

6.5 Increased NT Loading Levels

Although this project focused on low concentration of nanotubes to produce the polymeric conductor, experiments were carried out at various loading levels. The Winey dispersion procedure was used to produce samples made of MDPE with nanotube loadings from 10 weight percent (typical throughout the project) up to 90 weight percent. This direction into higher loadings was attempted to increase the probability of CNT-CNT contact within the conductor, allowing for a reduction in resistivity. The table below lists resistivity values obtained using this method.

Table 3 High weight % loading and resistivities

Weight Percent	Nanotube type	Resistivity (Ω·cm)
50	CG100	1.4×10^{-1}
60	CG100	6.0×10^{-2}
90	CG100	3.0×10^{-2}

The samples demonstrated similar bulk attributes across the samples and the optimization of the CNT-CNT connections reduced the resistivity.

6.6 Post Processing Treatments (NT-NT Connections)

6.6.1 Nanotube Terminations

The set up used for alignment studies is shown below in Figure 6. The samples were placed between two leads and connected to the power supply. The leads were listed as terminations. Three types were used, multi-stranded copper wire, single-core copper wire, and etched and silver coated copper wire. Three different terminations were used to reduce the contact resistance and improve the surface area of contact with the CG-SWNT / MDPE composites.

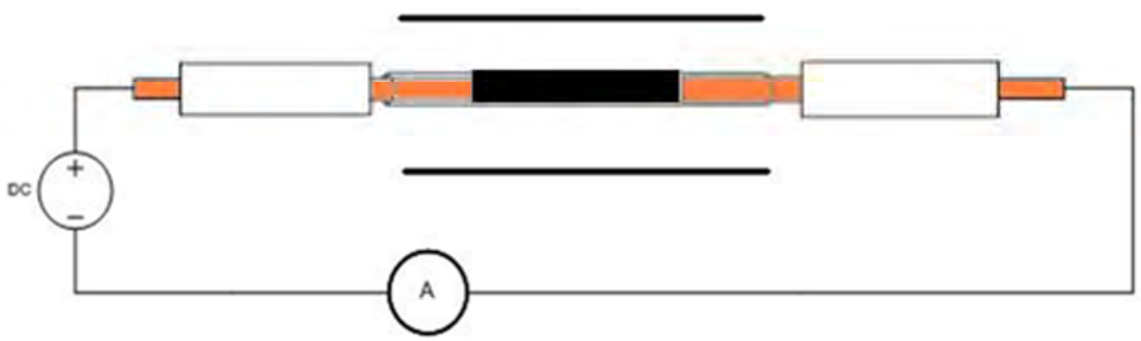


Figure 6 Electric field conditioning set up for polymeric conductors

Table 4 below shows the resistivity values obtained for different samples and terminations. No major change in the resistivity was observed due to change in terminations, however the number of runs required to condition the samples was reduced by using a single-core or silver coated wire as compared to the multi-stranded wire.

Table 4 Composite resistivity values under the effect of electric field

Sample AWG 8 – 18 strand copper wire as leads	Resistivity ($\Omega \cdot$cm)	Diameter (cm)	Electric Field Application
Polyethylene (MDPE)	10^{15}	0.394	None
10 wt% CG / MDPE	~ $1* 10^{3}$ – $1.5* 10^{3}$	0.394	None
10 wt% CG / MDPE	~ $4*10^{-2}$ – $6*10^{-2}$	0.394	At high temp
10 wt% purified HiPco / MDPE	~ $2*10^{-2}$ – $6*10^{-2}$	0.394	At high temp
10 wt% CG / MDPE	~ $5 * 10^{-1}$ – 10	0.394	At room temp
10 wt% purified HiPco / MDPE	~ $2 * 10^{-1}$ – 5	0.394	At room temp
10 wt% purified HiPco / MDPE **Single core copper lead*	~ $7 * 10^{-2}$ – $9* 10^{-2}$	0.394	At high temp
10 wt% purified HiPco / MDPE	~ $4.5 * 10^{-1}$ - $8 * 10^{-1}$	0.200	At high temp
10 wt% CG / MDPE **Silver coated copper leads*	~ $3.5*10^{-2}$ – $5*10^{-2}$	0.394	At high temp

6.6.2 Electric Field

To improve the electrical conductivity of MDPE/CG-SWNT composites, one of the post processing steps used was the application of an electrical field. Previous studies have shown that the SWNTs in a liquid behave as dipoles when subjected to an external electrical field and over a period of time, they tend to align in the direction of the field [6]. The electric field was used to improve the CG-SWNT network formation in the composite and also to reduce the polymer–carbon nanotube contact junctions that reduce the electrical resistivity of the composite. A schematic of the set up is shown above in Figure 6. The samples were heated to 145°C to let the polymer flow which in turn enables free rotational and translational motion of the SWNTs under the effect of electric field. The samples were conditioned 3 to 4 times which minimized the voids and improved the

current carrying capability of the composite. A low DC field with a voltage varying from 1 to 8 volts was applied. Several solutions used to combat the challenges that occurred are shown in Table 5.

Table 5 Electric field processing challenges and solutions for CG-SWNTs/MDPE composites

	Challenge	Solution
1	For CNTs to effectively align in the polymer, the polymer has to have low viscosity **Resistivity (~ 200 Ω·cm)**	Composites were heated to 145 °C to allow the nanotubes to align and form a network **Resistivity (~ 2.5 Ω·cm)**
2	For the electric field to be effective there should be a solid contact between the copper leads and the sample **Resistivity (~ 2000 Ω·cm)**	The sample was compacted between the leads by applying pressure and the leads were clamped in place **Resistivity (~ 60 – 100 Ω·cm)**
3	Unlike all previous studies where the polymers are either photo curable and UV curable, PE is not UV curable or photo curable **Resistivity (~ 50 – 100 Ω·cm)**	A low voltage electric field was applied when polymer was allowed to harden after alignment tests **Resistivity (~ 0.5 Ω·cm – 10 Ω·cm)**
4	Void formation will prevent a continuous network for electron flow **Resistivity at 145°C (~ 2.5 – 5 Ω·cm)**	Samples were conditioned and after each conditioning run the leads were pushed in further to eliminate the voids **Resistivity at 145°C (~ 0.02 – 0.09 Ω·cm)**
5	Upon applying force on the copper leads, the polymer flows on the exterior of the leads due to a minor difference between the inner diameter of quartz tube and the copper leads. This decreases the amount of polymer between the leads.	Sealing the area between the copper lead and inner diameter of the quartz with Teflon and holding the copper in place using an insulating tape and clamp reduced the polymer flow.

Figure 7 shows the current voltage statistics of a typical electric field conditioning test for the CG-SWNT / MDPE composites. It can be seen that after every conditioning run the current carrying capability of the composite is improved. This is because of improved junctions between carbon nanotubes and reduction in void formation.

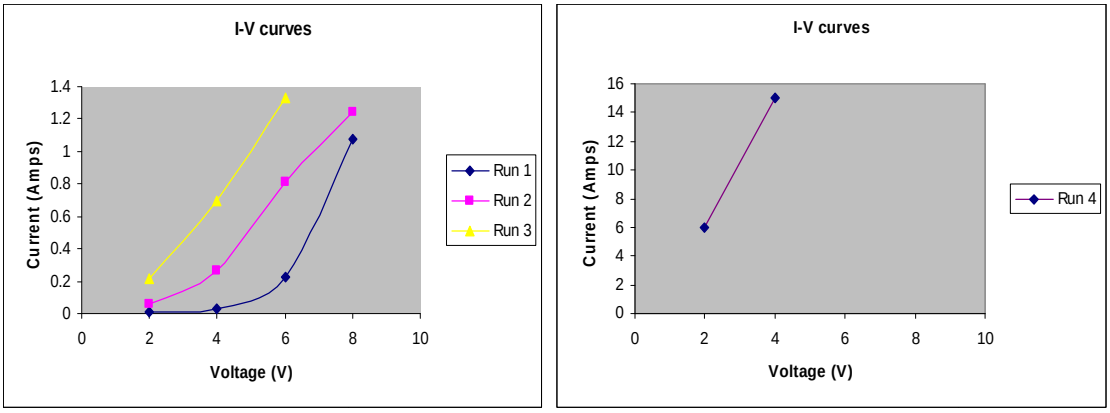


Figure 7 Current carrying capability of 10 wt% CG-SWNTs/MDPE composites based on voltage

Figure 8 and Figure 9 show SEM images of the composite before and after electric field processing. After electric field application, some areas of alignment were visually observed.

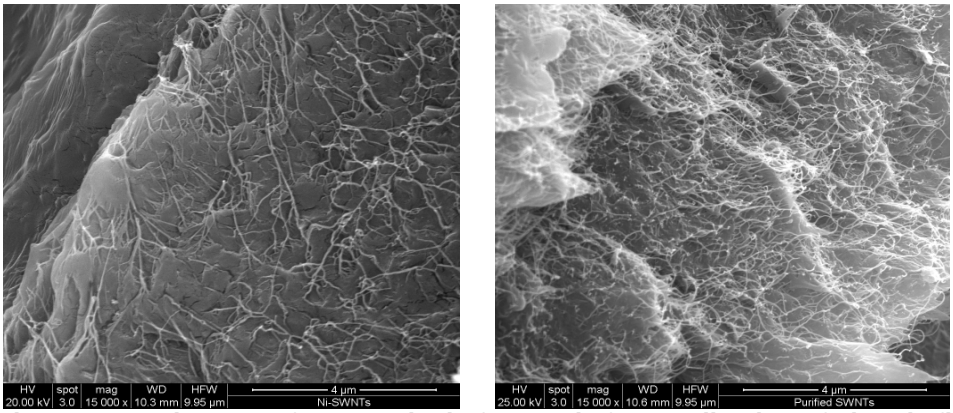


Figure 8 SEM images of composite before and after application of electric field

Before Electric Field **After Electric Field**

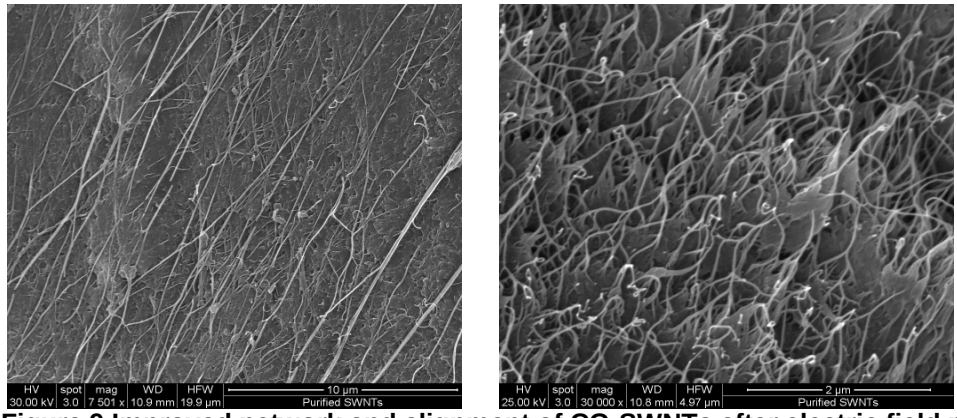


Figure 9 Improved network and alignment of CG-SWNTs after electric field processing

6.6.3 Annealing

Annealing is a method used to enhance the conductivity of the composite wires. The effect is more pronounced for low loading samples than for high loading samples. Figure 10 shows that annealing causes the conductivity of the composite wires loaded with 10 wt% nanotubes to increase by two orders of magnitude. For higher loading samples, the enhancement effect dims at the same annealing condition.

Annealing is typically done post-processing for 40 minutes in a vacuum oven set at 115ºC. The oven is then turned off and the sample is cooled slowly to room temperature.

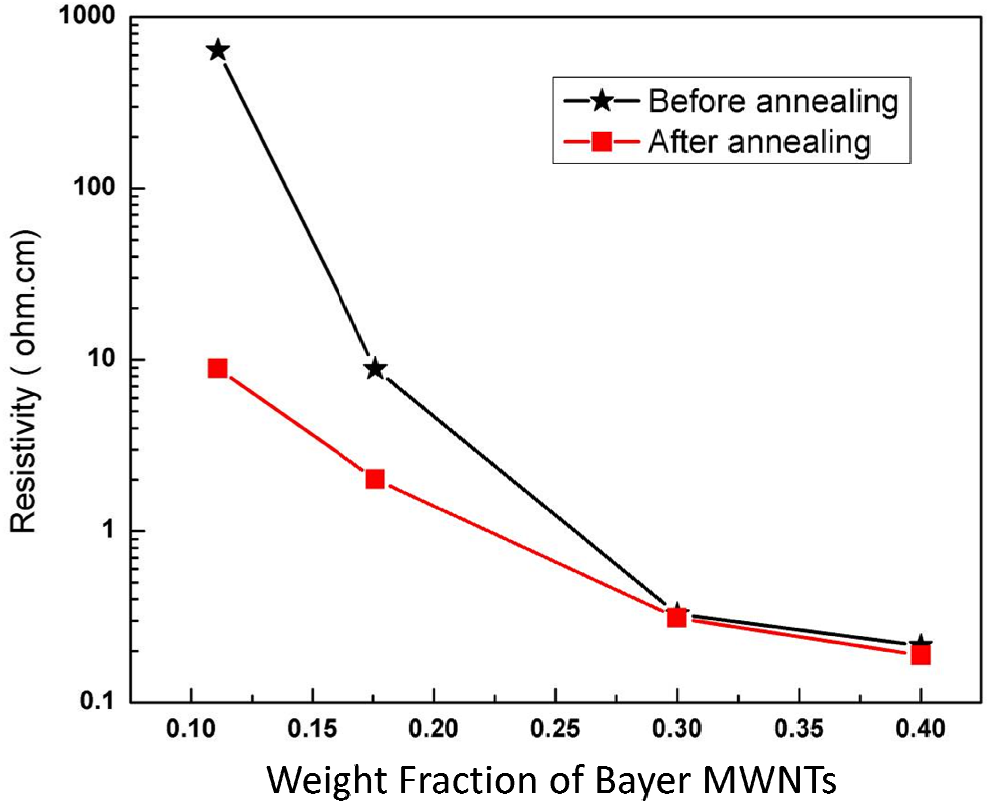


Figure 10 Annealing impact on resistivity of Bayer MWNTs

6.6.4 Pressure

Direct contact of the nanotubes in the composite is one of the key factors in approaching the desired conductivity of the CNTs/polymer composites. Motivated by the promising scenario that polymers between nanotubes are squeezed out and direct contacts between nanotubes can be realized, various pressures were applied on the as-produced wire samples using a hot press in the uniaxial direction. The equipment can supply desired pressures while maintaining the sample in a softened state by homogeneous heating. Table 6 shows the resistivity of the samples before and after compression by 3000 Psi pressure at 150°C. The resistivity was measured at room temperature. The compression resulted in a decrease in resistivity of about 5 percent for the samples with 30 wt% loading of MWNTs with respect to the un-compressed sample. The pressure was increased to 30000 Psi and the resistivity of the sample was reduced by as much as 15 percent with respect to the un-compressed counterpart.

Table 6 Resistivity of the composite before and after compression

	Initial Resistivity (Ω·cm)	**Resistivity after Compression (Ω·cm)**
30 wt% Loading	0.38	0.36
40 wt% Loading	0.14	0.13

6.6.5 Doping/Intercalation

Intercalation is a term used to describe the reversible incorporation of a foreign molecule between two other molecules, most often in a periodic structure. It is most associated with the incorporation of foreign species between layers of graphite hence the term; graphite intercalation compounds (GICs).

The introduction of foreign species to carbon nanotubes is more commonly described as *doping.* Doping in this sense can be broken down into three main categories [7]:

(a) Endohedral inclusion of the free space within the nanotube
(b) Replacement of carbon atoms of the nanotube structure with a dopant
(c) Exohedral incorporation of molecules between nanotubes within a bundle or agglomerate

The exohedral doping correlates closely to the intercalation of graphite, in particular when a charge transfer between dopant and nanotube often lead to novel electrical properties [7, 8].

For this initial study, several dopants were investigated: iodine, thionyl chloride, and antimony pentafluoride. The first dopant was applied to an extruded composite wire and produced a decrease in resistivity of 67%. The remaining two dopants were applied to the nanotubes prior to integration into the polymer matrix. The thionyl chloride reduced the resistivity of the sample by 50%. The antimony pentafluoride showed an increase of the nanotube conductivity by over one order of magnitude, but further research is needed to incorporate the doped nanotubes into the polymer matrix to determine the effect on the composite. Each of these methods is discussed below in further detail.

6.6.5.1 Iodine Doping

Composite wires were doped using a post-processing treatment. The as-produced composite wires were placed in an iodine steam environment for 8 hours. Upon removal, the resistivity of the treated composite wires reduced by 67%. The sample with 30 wt% loading ratio reduced its conductivity from 0.48 Ω·cm to 0.16 Ω·cm. Although a reduction in resistivity was observed, it is unclear how much of the improvement can be solely attributed to iodine atoms.

6.6.5.2 Thionyl Chloride Doping

Thionyl chloride, SOCl2, was used as a dopant to make the nanotubes more conductive and facilitate their dispersion within the polymer matrix. Before adding the nanotubes into the HDPE matrix, the nanotubes were doped by SOCl2 [9, 10, 11]. 5 g raw Bayer MWNTs were added into 50 ml SOCl2 solvent. The solution was heated to 150°C and maintained at that temperature for 2 hours. Following filtration and washing with copious amounts of water, the SOCl2 doped MWNTs were collected and dried in an oven at 105°C overnight. The SOCl2 doped nanotubes were then used to produce the composite wire. The composite wires loaded with SOCl2 doped CNTs showed 50% increase in the conductivity compared to its counterpart loaded with pristine CNTs at the same loading ratio.

6.6.5.3 Antimony Pentafluoride

Single wall carbon nanotubes (SWNT) and SbF_5 were combined in a method based on Lalancette *et al.* [12]. The SWNT were dried by heating under vacuum in a boiling flask for 72 hours at a temperature range of 90 – 110°C. The sample was transferred to a plastic glove bag for processing under an atmosphere of dry nitrogen. SbF_5 (Sigma Aldrich) was pipetted onto the SWNT inside a boiling flask. The end product was a dry black powder,

similar to the starting SWNT, which appeared stable under normal atmosphere and was resistant to hydrolysis.

In order to measure electrical conductivity, the small amount of material produced dictated the use of a simple two-point probe measurement. The material was placed inside a Teflon tube and a probe attached at each end. Two-point electrical probe measurements were obtained using a Commercial Electrical HDM350 Multimeter with the following results:

Table 7 Antimony pentafluoride doping results

Tube Type	Resistance (Ω·cm)
Raw SWNT	55.3
SWNT SbF5	2.3

The SbF_5–treated SWNT showed over an order of magnitude improvement in conductivity. This is in keeping with the typical factor of ten improvement noted by Inagaki *et al.* review [13].

The sample showed a mix of two tube types, but the microscopy consistently found very rigid and straight nanotubes in the 20-40nm range (Figure 11). High-resolution STEM images of the smaller ~2nm nanotubes suggest these are modified or functionalized SWNT (Figure 12). Energy Dispersive Spectrometry (EDS) data shows the presence of C, Sb and F (Figure 13) on these smaller nanotubes.

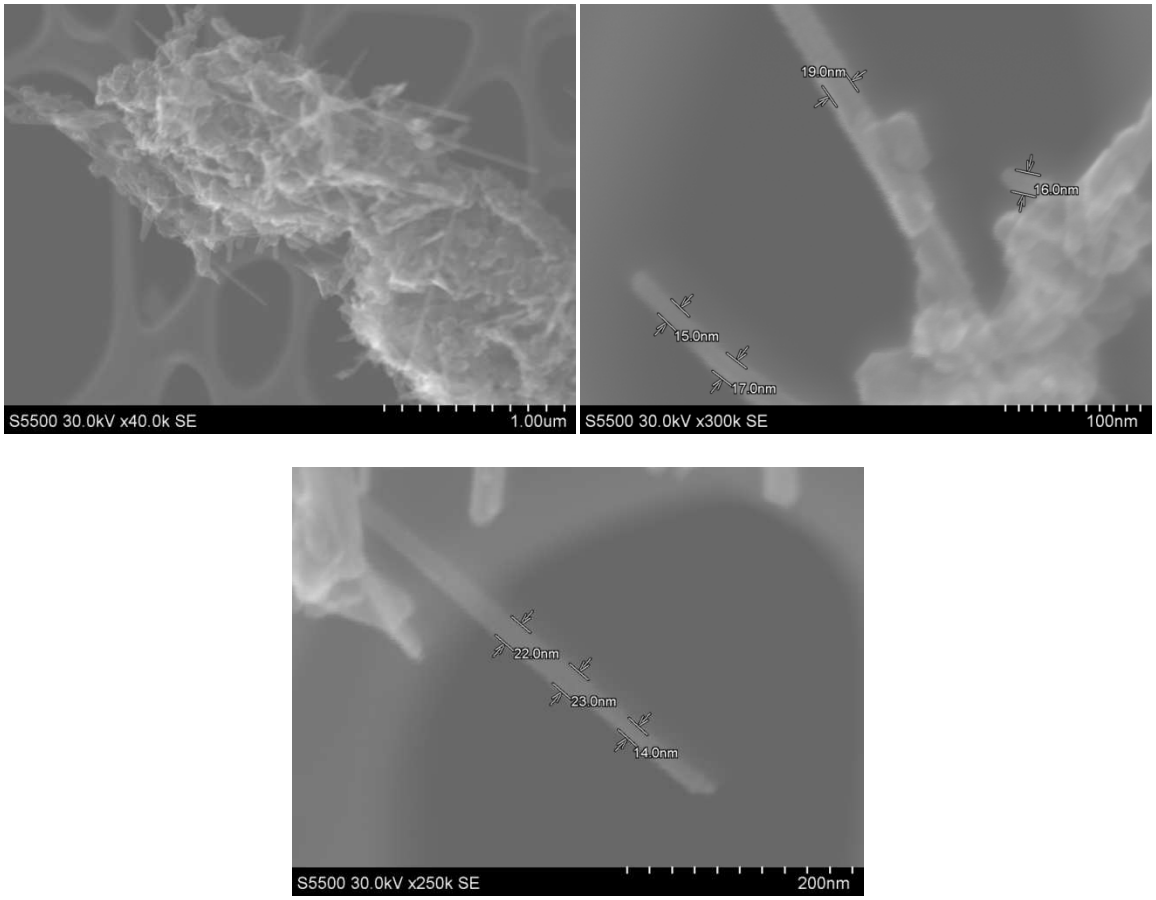


Figure 11 STEM imagery of material produced with high resolution images of large diameter tube structures

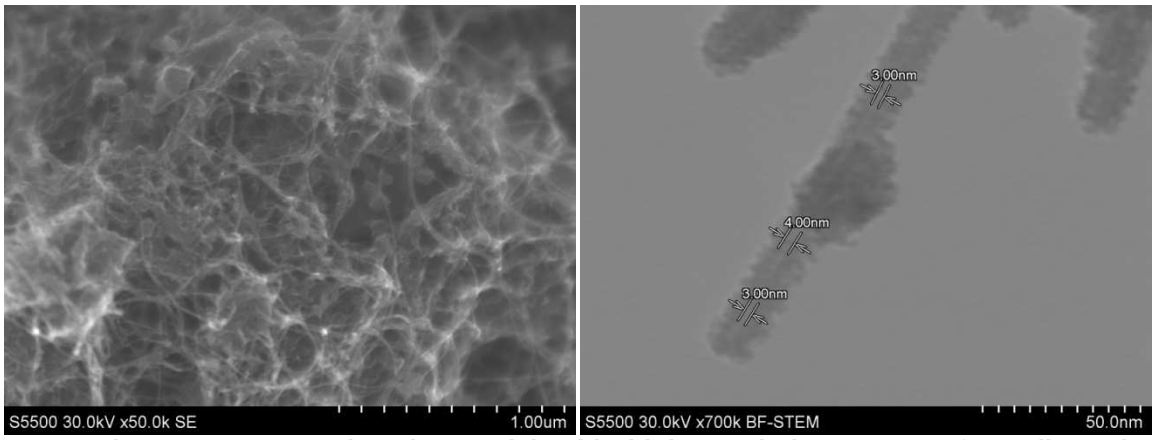
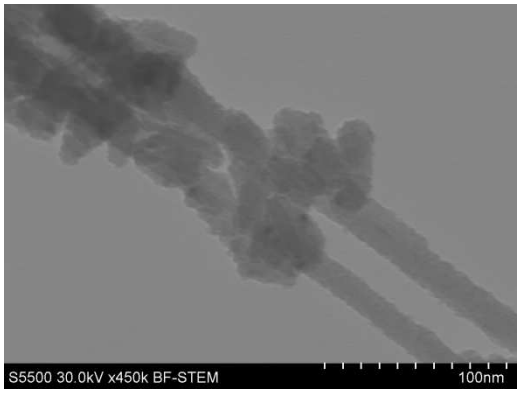


Figure 12 As produced material with high resolution STEM of smaller tube structure. Surface morphology of small tube shows definite changes over raw SWNT



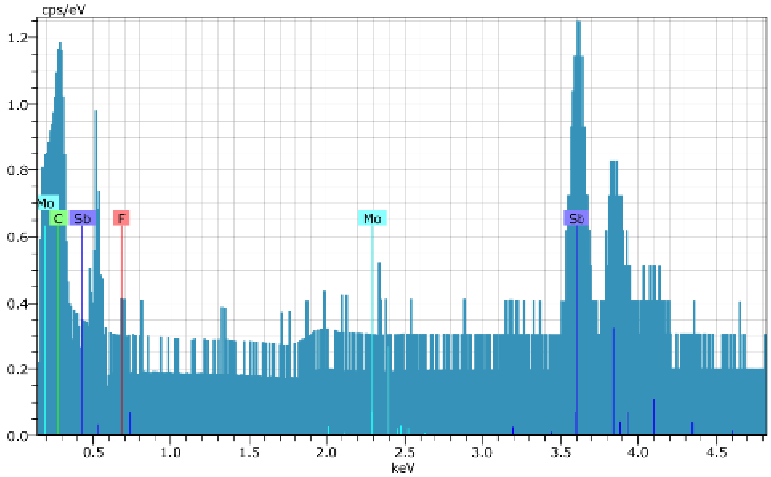


Figure 13 STEM image of coated small tube structure and corresponding EDS data confirming presence of C, F, and Sb

Figure 14 and Figure 15 further highlight the presence of C, Sb and F through EDS area scans and STEM microscopy.

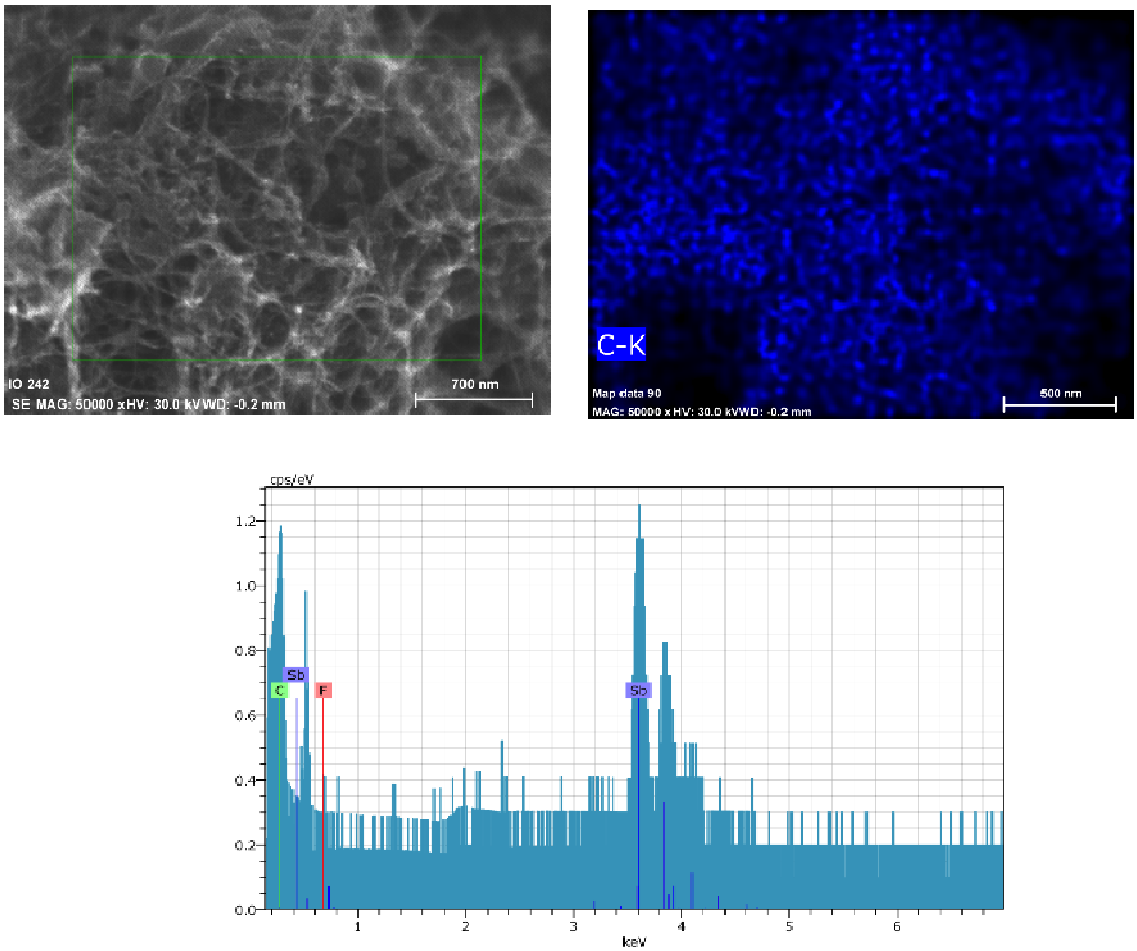


Figure 14 SEM and corresponding EDS area map of carbon nanotube bundles showing presence of C, Sb and F

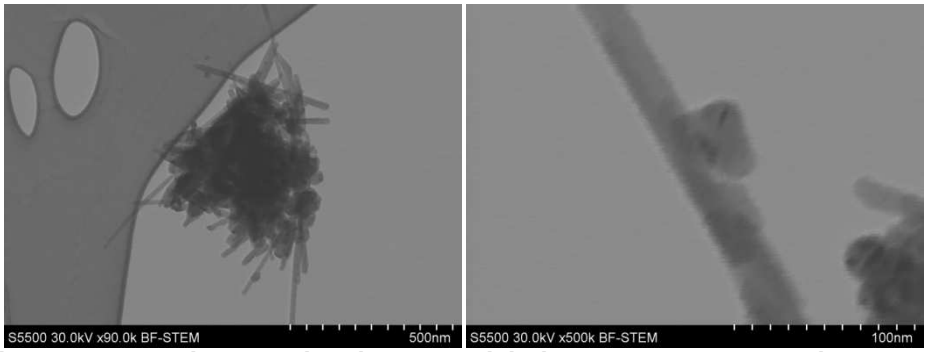


Figure 15 STEM images showing potential Sb presence on nanotube

6.6.6 Metal Additives

Simpler than chemical doping or coating is the incorporation of nanoscale metal particles into the CNT polymer composite to increase interconnectivity of the nanotube network (Figure 16).

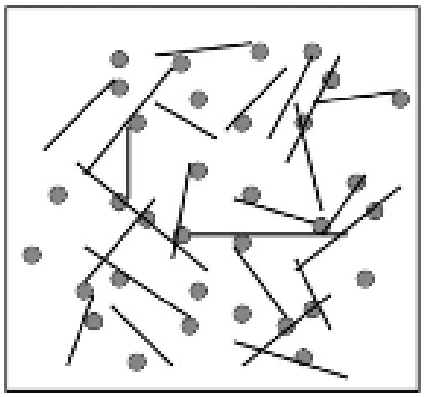


Figure 16 Illustration of increasing interconnectivity of nanotube networks [14]

In an effort to harness the potential for more facile processing suitable for bulk fabrication, a number of potential protocols were explored. SWNT and MDPE were combined with both aluminum oxide and silver nanoparticles (Figure 17 and Figure 18). The composites that included aluminum were exposed to microwave energy in an effort to perform in-situ removal of the thin oxide layers present.

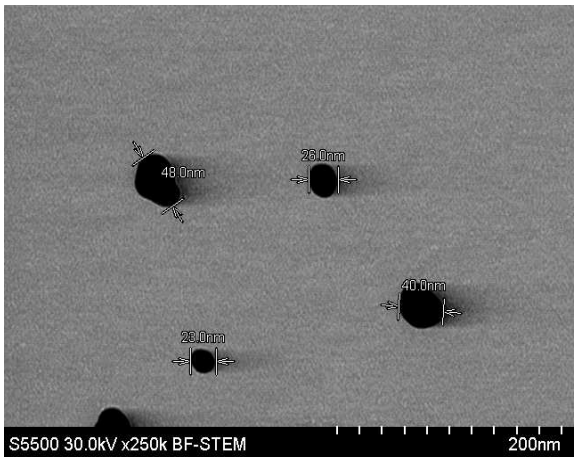


Figure 17 Silver nanoparticles

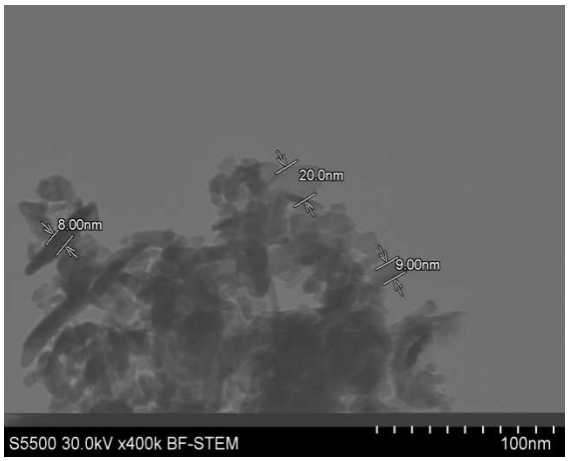


Figure 18 Aluminum nanoparticles

Composites comprising 10 wt% SWNT in MDPE showed improvements using 0.1 – 1 wt% of silver nanoparticles of one order magnitude or less in resistivity.

6.6.7 Microwave Processing

A research group at Rice University has shown the heating effect of carbon nanotubes (CNT) with microwaves to be highly efficient, even when included in a polymer to form a composite [15, 16]. Higginbotham, Moloney et al have shown that even less than 1 wt % of CNT included in a ceramic composite can be heated in excess of 1000°C in minutes using 30-40 watts of microwave energy [17].Conductive polymer composites containing CNT, whose conductivity has been further improved by a microwave process, would be very useful for umbilical applications. This microwave process is a low cost, highly scalable procedure that can improve the electrical conductivity (reduce resistivity) of CNT polymer composites (patent pending). The experiment resulted in a reduction in resistivity by 33% and is further described below.

6.6.7.1 Experimental

CNTs were dispersed in polymers (PE, PEEK, PS) by mechanical and/or chemical means. These CNT-polymer nanocomposites were exposed to microwave radiation either in an S-Band wave guide or a simple microwave oven. The nanotubes heated rapidly and the polymer in their immediate vicinity is modified creating conductive pathways between each nanotube, which in turn increases the interconnections between the nanotubes and reduces the bulk resistivity of the composite.

The resistivity of CNT polymer composites can be reduced to as low as $1*10^{-2}$ Ω·cm via mechanical, chemical and electrical processing. Often, these steps are costly, time consuming and not scalable from the laboratory to industrial usefulness. By harnessing the heating effect of CNTs, a novel process for the enhancement of CNT polymer composite conductivity (reduction in resistivity) has been observed. It is thought this reduction in resistivity is due to either:

(1) Polymer char between the CNT providing increased electrically conductive pathways or
(2) Polymer char between the CNT providing increased electrically conductive pathways *in combination with* movement and alignment of the CNT due to the melting of the polymer and electromagnetic forces placed on the CNT by the microwave radiation (see Figure 19).

CNT polymer composites tested include:

- Single wall carbon nanotubes (SWNT) and polyether ether ketone (PEEK)
- SWNT and high density polyethylene (HDPE)

- Multiwall carbon nanotubes (MWNT) and MDPE

6.6.7.2 Characterization and Results

Reduction in resistivity of 33% has been observed using an S-band wave guide producing 70 watts of microwave energy for exposures of less than 30 seconds. The composite bulk mechanical properties remained unchanged post microwave treatment.

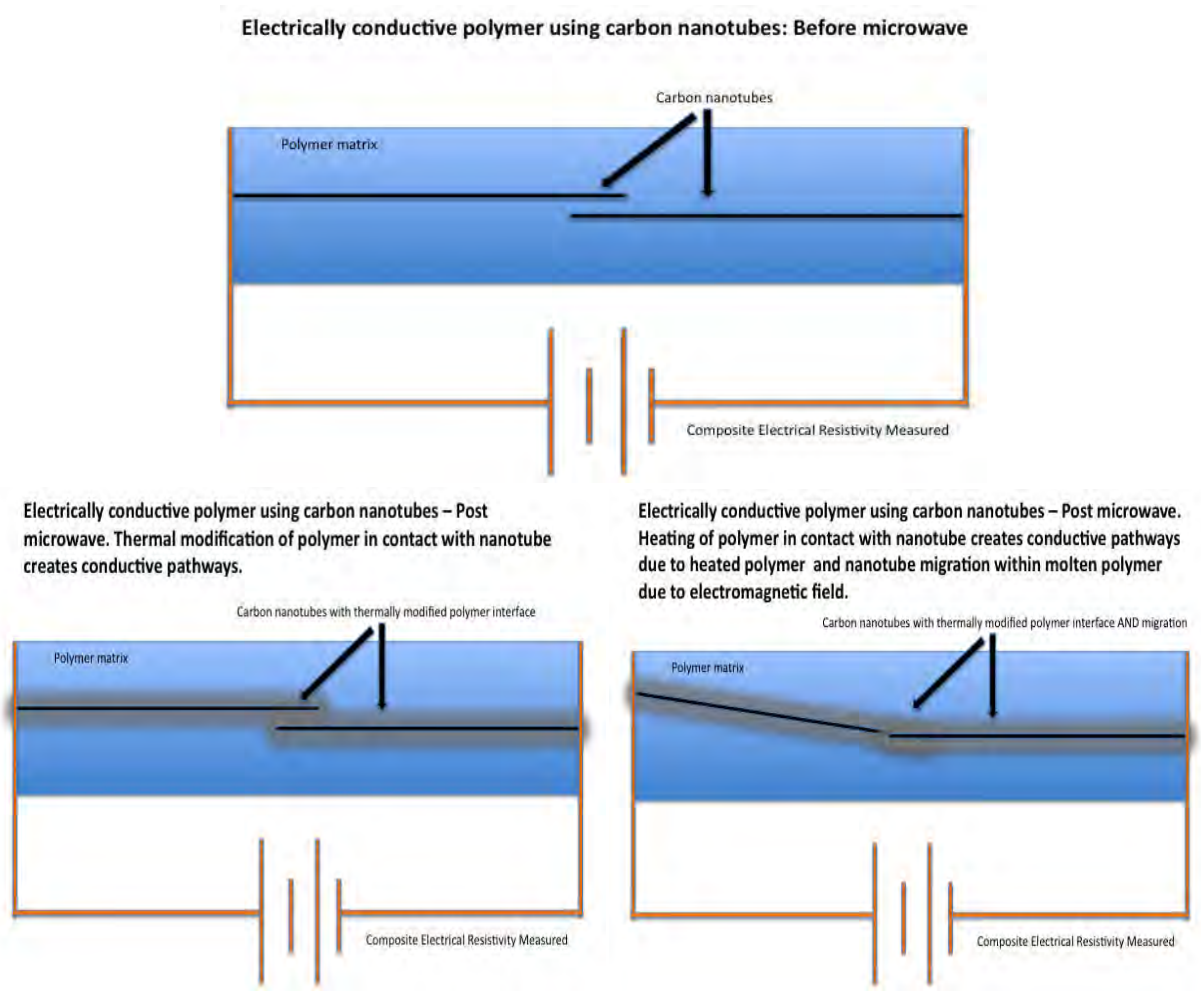


Figure 19 Conductive pathways before and after microwave processing

The heating effect of nanotubes from microwave radiation is not fully understood. These initial experiments showed that further refinement of the process, with more control on the microwave exposure, would be useful. Initial testing showed that the bulk mechanical properties remained unaffected by the microwave heating.

7.0 COST ANALYSIS OF THE CONDUCTOR AT LONG LENGTHS

The eventual cost of the PNU cable will be dominated by the cost of the metallic single wall nanotubes (m-SWNTs) which will need to be employed in the final product. As the cable is currently conceived, the matrix material will be a polyethylene (PE) polymer. Various forms of PE are commonly used throughout industry and are readily available. They are a commodity product whose cost varies with the cost of petroleum products, and for the purposes of this report the price assumption will be in the range of $2.00/lb.

The cost of the nanotubes is a much more challenging proposition with costs ranging from $0.50/gram to as high as $200,000.00/gram. This wide variation is caused by the variation in the types of tubes. The low end cost is for commonly available multiwall nanotubes, with the high end being for enriched metallic single wall nanotubes. Of course, the metallic single wall tubes are expected to be needed for the final product.

If the PNU cable achieves the ideal conductivity goal as stated for the project, the cable will have four times the conductivity of copper. Since the polymer/nanotube density is ~1/9th that of copper, a unit mass of PNU will produce 36X's the length of wire as an equal mass of copper. Today, a pound of copper costs ~$3.50, 36 pounds would cost $220.00. Assuming our eventual nanotube cost will be $100.00/gram, one pound of PNU (equivalent wire length for 36 pounds of copper) would cost ~$4500.00 (10 wt% nanotubes in PE). The cost of the polymer is negligible for this cost estimation as well as the manufacturing cost for turning the polymer/nanotube material into a wire. It is also assumed that the manufacturing cost of turning copper into wire and PNU into wire is equivalent. For cost equivalence, the price of the nanotubes will have to drop to ~$4.00/gram. This would seem to be a huge price decline, but with increased production of nanotubes throughout the world it is not unimaginable, as was seen with the cost of carbon fiber ($1000/lb to $10/lb). Also, this estimation does not include any cost benefit for the product, which should be significant.

8.0 SUMMARY OF RESULTS AND REMAINING TECHNICAL HURDLES

While the original scope of this study was to design, build, and test a prototype of a polymeric conductor in its most ideal form, this project ultimately produced two prototype specimens that were demonstrated during the nano-Umbilical Workshop. The first sample measured one foot in length, 2mm in diameter, and was shown to power a light bulb (comparison study). A picture of the setup is shown below in Figure 20. The second sample was in a glass tube approximately 5 cm long and was used to power a pump, as shown in Figure 21 below.

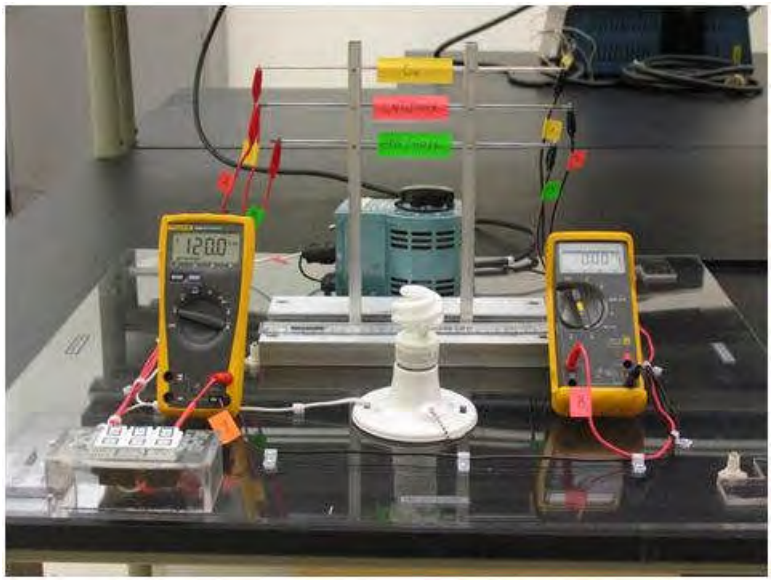


Figure 20 Setup of polymeric conductor prototype

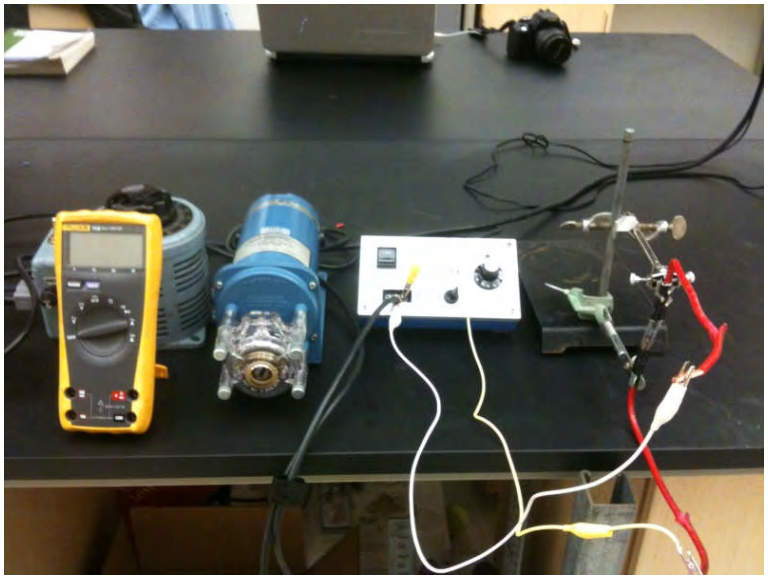


Figure 21 Setup of sample used to power pump (higher voltage condition)

Polymeric Conductor Properties Achieved:

- Lowest resistivity value reached in the melt state was $2*10^{-2}$ Ω·cm.
- Highest voltage carried by PNU was 40V (the limit has not been evaluated).
- Highest current carried by PNU was 16 A (not fully optimized).
- Identified several new steps for lowering resistivity.
- Nanotube concentrations up to 90 wt% were evaluated.

Although the polymeric conductor was not produced in its ideal form, seventeen orders of magnitude improvement from the standard polymer material was realized. It is expected that with the use of more metallic SWNTs a much higher level of conductivity may be achieved. In addition, many of the new methods used during this study should be further advanced, potentially enabling new technologies.

As shown in the table below (Table 8), many of the program tasks were achieved and led to sample pieces for two setups (two experimental stations) to demonstrate polymeric conductors.

Table 8 Status of program tasks at the end of the one year program

Technical Tasks (Monthly)	Completion Date	Status
a. Obtain SWNTs & m-SWNTs	May	Completed
b. Process wires w/ polymer 1 & 2	April	Completed
c. Test properties of 1 & 2 wire	April	Completed
d. Characterize m-SWNTs	May	Completed
e. Conduct NT-NT study	September	*Incomplete*
f. Improve NT-NT conduction	September	Completed
g. Disperse SWNTs in 1 & 2	April	Completed
h. Disperse m-SWNTs in 1 & 2	October	Completed
i. Implement Electric Fields	November	Completed
j. Characterize NT filled wires	December	Completed
k. Conduct physical tests	December	*Incomplete*
l. Connection study	December	Completed
m. Reporting	Monthly	Completed
Milestones	**Completion Date**	**Status**
1. Obtain m-SWNTs	March	Completed
2. Produce first 1 ft wire	June	Completed
3. Evaluate for umbilical	September	Completed
4. Evaluation & optimization	September	Completed
5. Optimize and prototype test	December	*Incomplete*
6. Final Report	December	Pending
7. nano-Umbilical Workshop	December	Completed

Listed below are a number of items identified and discussed as technical/engineering hurdles that remain that could be overcome in continued implementation of this program. The hurdles involve overcoming scientific aspects that will enable the PNU to reach lower resistivities and longer lengths.

The hurdles to overcome are as follows:

(1) Reduce or eliminate the phenomenon of nanotubes becoming individually coated with the host polymer. Novel methods to accomplish this are needed.

(2) The minimum achievable resistance between the nanotubes has not been formally tested. A NT-NT contact study should be completed to determine this resistance.

(3) Determine the effect of contact angles and overlap distance between nanotubes on electrical resistance.

(4) Determine the ultimate electrical resistivity of metallic versus non-metallic single wall nanotubes.

(5) Optimize the processing methods employed to achieve best possible conductivity. This includes high dispersion and improved alignment of nanotubes, use of pressure and doping to enhance contact of nanotubes, and review of the complete manufacturing process.

As the knowledge base regarding nanotube composite polymeric conductors continues to expand, several intermediate products may be discovered while working toward the ultimate goal of the polymer nanotube umbilical.

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APPENDICES

Appendix 1, Acronyms and Abbreviations

CG	Commercial Grade
CNT / NT	Carbon Nanotube / Nanotube
DCB	Dichlorobenzene
DMF	Dimethylformamide
ESD	Electro static disipation
EMI	Electro magnetic interference
GICs	Graphite Intercalation Compounds
HD	High Density
HiPco	High Pressure carbon monoxide
LD	Low Density
m-SWNTs	Metallic Single Walled Carbon Nanotubes
MD	Medium Density
MWNT	Multi Walled Carbon Nanotubes
NMP	n-methylpyrrolidone
PE	Polyethylene
PNU	Polymer Nanotube Umbilical
PS	Polystyrene

SEM	Scanning Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
SWeNT	Southwest Nano Technologies
SWNT	Single Wall Carbon Nanotube
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis

Appendix 2, Presentation slides from nano-Umbilical Workshop

Slide presentations included:

NanoRidge Corporate Overview

Ultra-High Conductivity Umbilicals

Conduction with Nanotubes (Materials Challenges)

Need for Lightweight Umbilicals

Paradigm Change in Electrical Conductors

PNU Properties at the nanoscale

Steps to Achieving Conduction

Steps to Manufacture the PNU

Outcomes

Corporate Overview

Contains NanoRidge Materials proprietary information

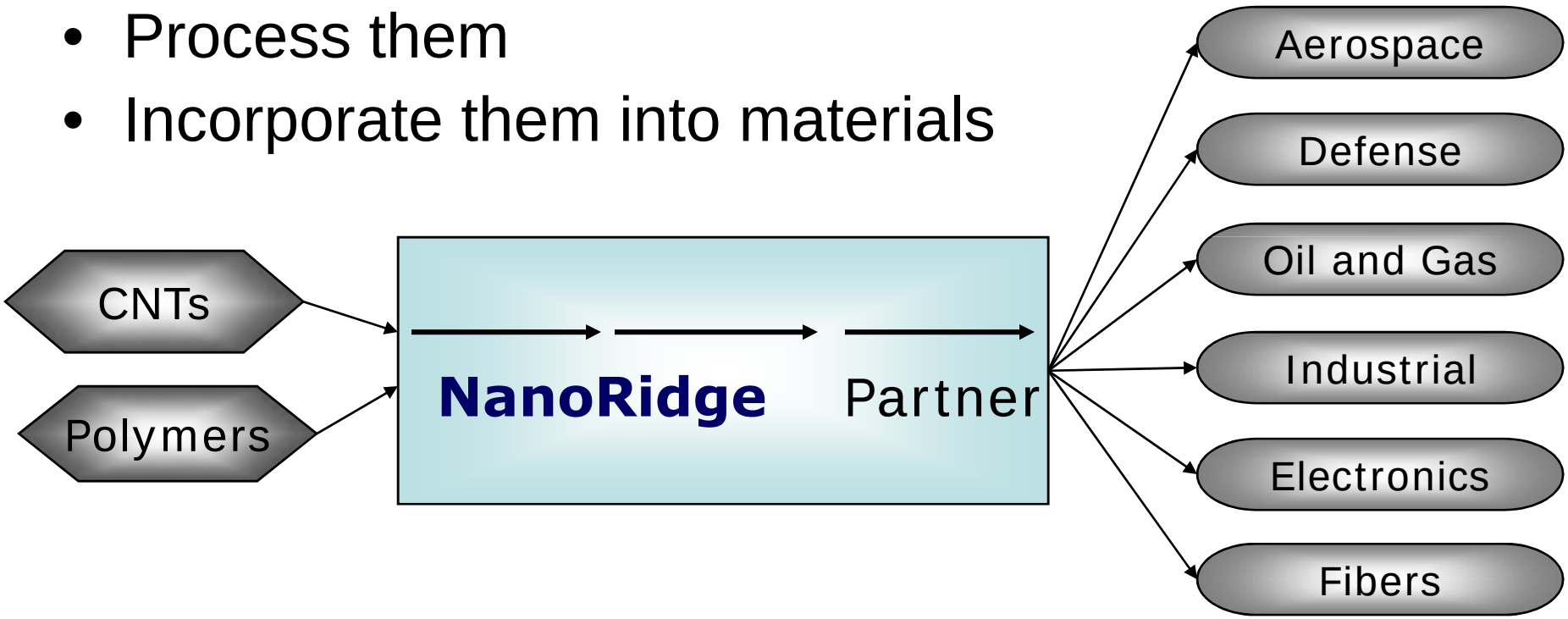
NanoRidge Overview

- Incorporated in 2004
- Licensed university technologies portfolio
- 12 full time employees
- Develop nano-enhanced materials for specific customer needs
- Manufacture chemically modified nanomaterials

NanoRidge

Where NanoRidge Fits In

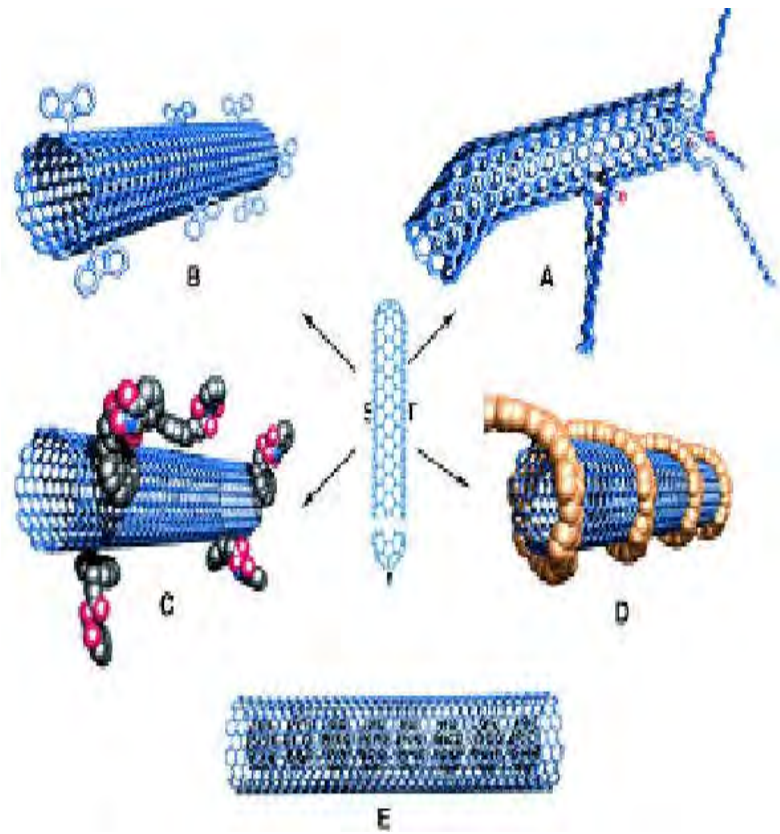
- Purchase nanomaterials
- Process them
- Incorporate them into materials



NanoRidge

Chemical Functionalization of Nanotubes

- Regarded as the key to efficiently exploiting nanotubes for mechanical reinforcement
  - Natural bundles must be dispersed
- Choice of functional group critical
  - Chemistry of carbon is extremely versatile
  - Functional group has major effect on resin property enhancement
- NanoRidge has strong foundational IP and industry-leading expertise in nanotube functionalization and incorporation into composites



Picture Source: Andreas Hirsch, 2002

NanoRidge

NanoRidge Technologies are the Key

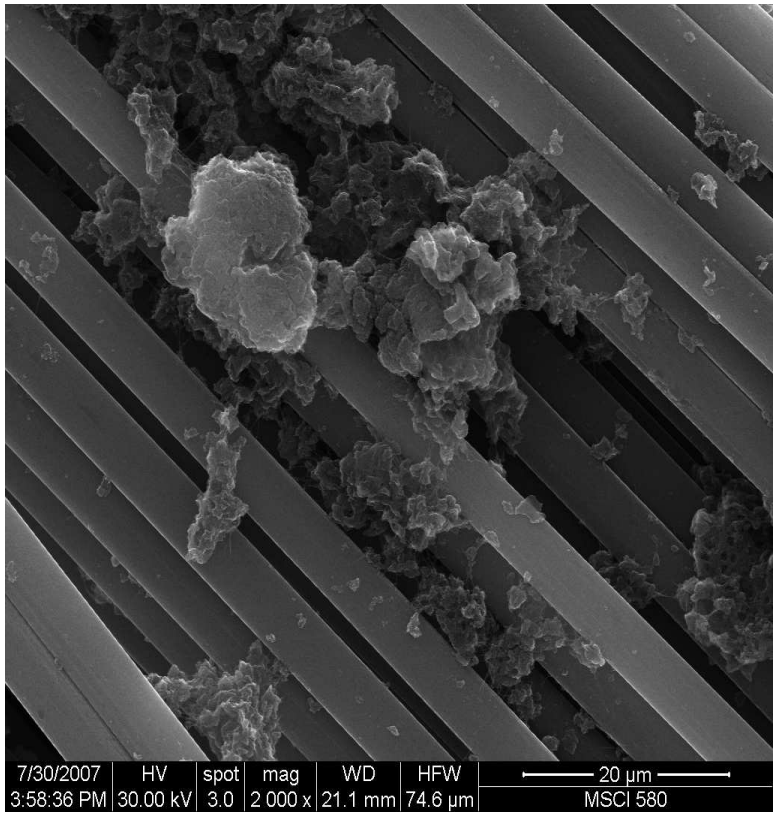


Figure A: As-received nanotube agglomerates "dispersed" on surface of fibers

NanoRidge

Processing

Technology

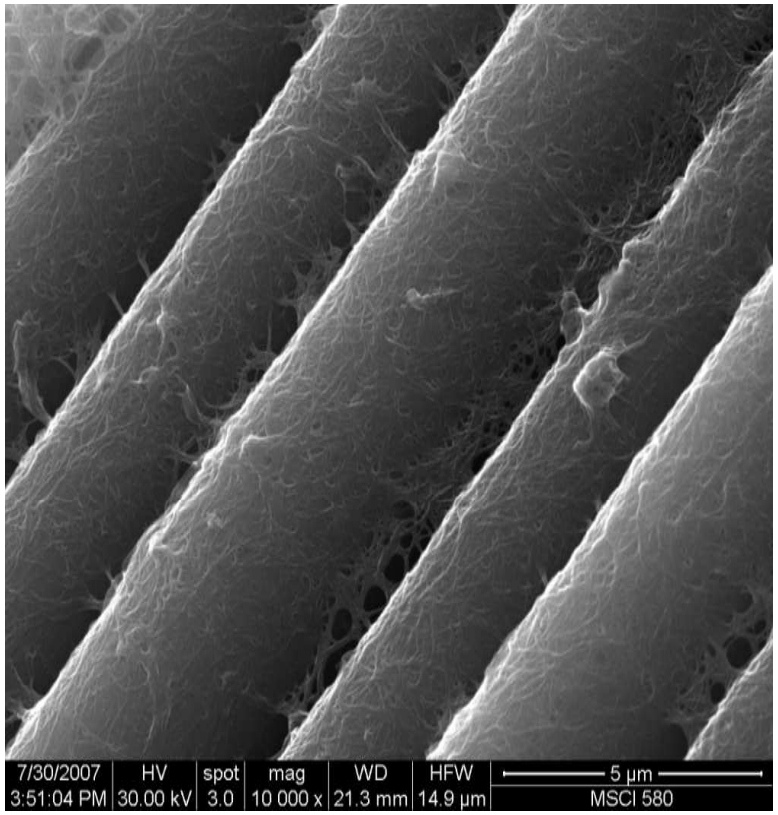


Figure B: NanoRidge functionalization and processing technologies result in uniform nanotube dispersion on fiber surface

NanoRidge

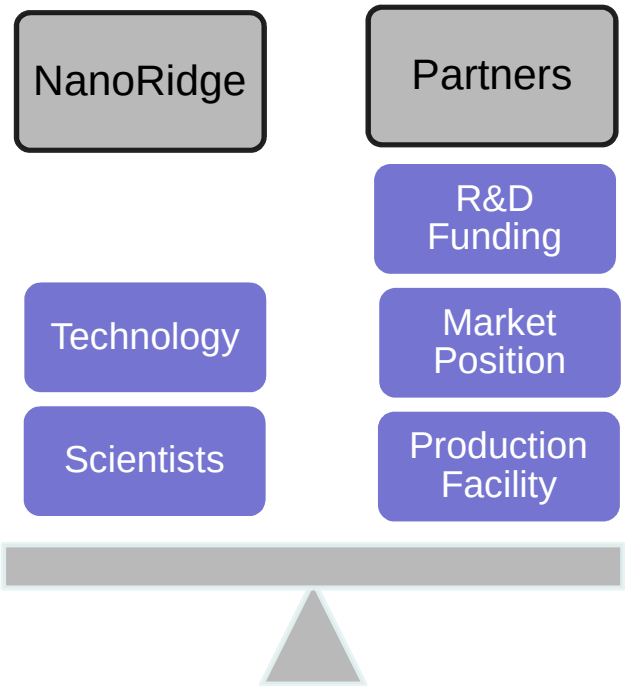
Key Technologies Owned

- Functionalization methods and products
- Polymers incorporating nanotubes
- Structural composites incorporating matrices with nanostructures
- Fibers with nanotubes in a composite structure
- Ceramics and metals incorporating nanotubes

NanoRidge

Corporate Strategy

Technology Leverage



Commercialization Pathway

Research & Development

Initial internal assessment

Factors involved:

Scalability

Return on investment

Economies of Scale

Joint Development

Partnership designed to develop product for given application

Often funded by partner

NanoRidge determines appropriate treatment for nano material

Project concluded with product tests

Joint Venture or Sublicense

Partnership formed to spell out the terms for product manufacturing

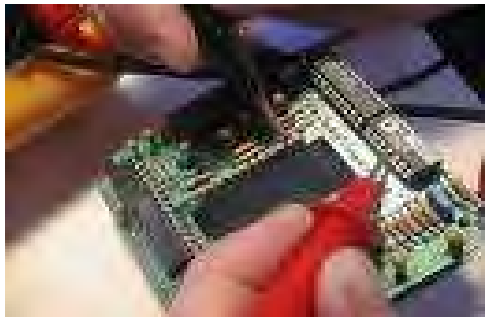
Joint Venture Agreement will determine % of ownership and contribution

Likewise, a sub licensee will have associated royalties, etc.

NanoRidge

Commercial Projects

- Aerospace / Tier 1 suppliers
  - Structural composites
  - Aircraft interior
- Armament
- Oilfield services
- Engineering resin (in-reactor modification)
- Industrial gaskets and pumps (elastomer)
- Electrically conductive plastic (aerospace, electronics)
- Hardened metal alloys



NanoRidge

Elastomers for Oil & Gas Applications

- Nanotubes act as “rebar” for rubber
  - Provides property improvements not achievable by formulation changes
- Functionalization chemistry and nanotube incorporation methods developed for several elastomer types
- Major potential customers identified
  - Positive response to physical property data
- Joint Venture with Zeon Chemical (2008)
  - Back-integrate functionalized nanotubes into industrial process in current pilot plant facilities
  - Customer application qualification in-process

NanoRidge

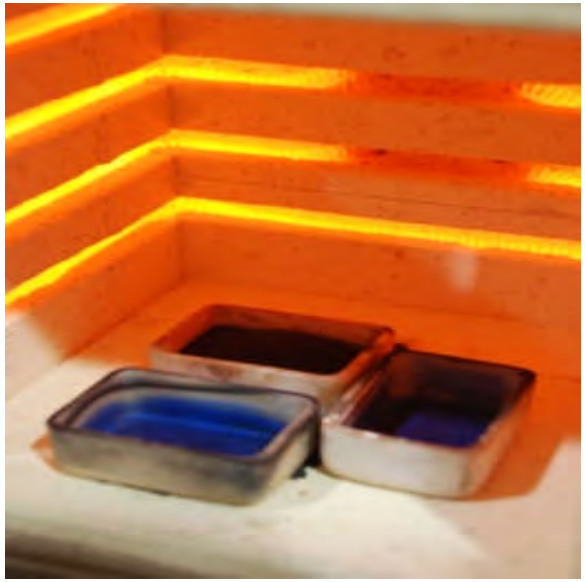
Structural Composites Improvements

- Tensile strength +20%
- Fatigue life >10X
- Impact resistance +300%
- Thermal conductivity +2X
- Higher operating temperatures

NanoRidge

Nanotube Metal Alloys

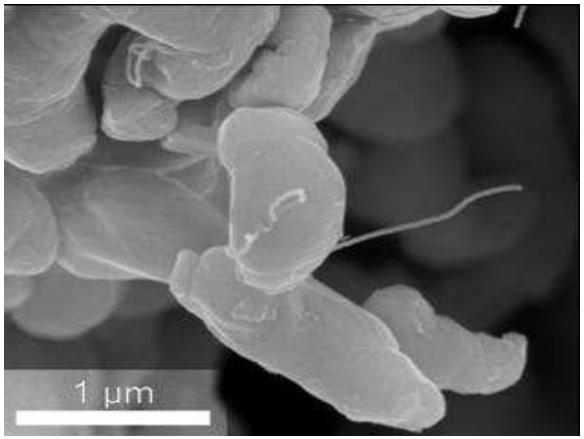
- Functionalize CNT's for compatibility with various industrial alloys
- Targeted physical property effects
  - Tensile strength
  - Young's modulus
  - Hardness (grain size modification)
  - Wear rate & coefficient of friction
  - Fracture toughness (crack arrest)



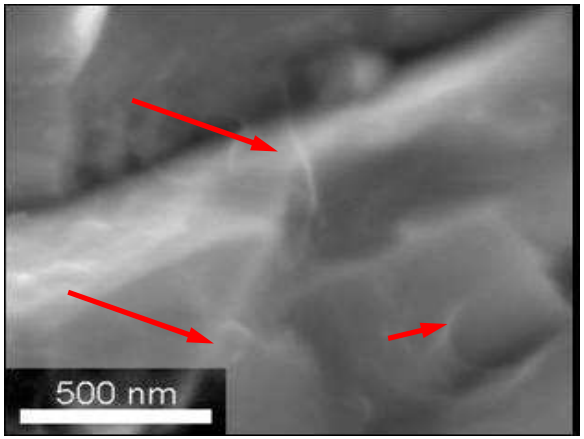
NanoRidge

Enhanced Alloys – Current Projects

- Matrix strengthening of tungsten-carbide alloys
  - Joint development with major oilfield services company
  - Goal is to increase wear life of drilling tools
  - NMI provides CNT-enhanced alloy compositions
  - M-CNT survivability proven; preliminary mechanical test results by end of 2009
- Hardening of SS alloys for surface durability
  - Goal is to increase wear life of alloy-clad steel parts
  - Test plan under review for sample fabrication
  - Functionalized CNT's developed for high-Ni alloys



CNTs dispersed on matrix powder



CNTs survive after sintering

NanoRidge

Air Force STTR

- Air Force sponsored research to enhance PAN-based carbon fiber with carbon nanotubes
  - **Collaborator:** New Jersey Institute of Technology
- Phase I investigated monofilaments as proof of concept
- Phase I results
  - Demonstrated improved mechanical properties

Sample	Load at Break (gf)	Tensile strain at Break (%)	Modulus (gf/den)	Tenacity at Break (gf/den)
Blank PAN	255	7	118.05	3.69
SWNT / PAN	462	10	143.15	6.17
% Improvement	81%	43%	21%	67%

Air Force STTR

- **Phase II Objectives:** Expand on Phase 1 successes → manufacture and test CNT-enhanced carbon fiber tows
- **Collaborator:** New Jersey Institute of Technology
- **Funding:** AFOSR, $750,000 for 2 years
  - Phase II awarded October 2009
  - Phase II commencement January 2010

NanoCable

A NanoRidge/Boeing Joint Development Project
Co-Funded by NIST-ATP

- Three year project to develop a lightweight electrically conductive polymer wire
- Utilize electrically conductive nanotubes embedded in a polymer matrix
- Markets: Aircraft, Satellites, Offshore Oil Production, Power Transmission, Electronics
- ATP award of $2.8MM, total project cost = $5.8MM

NanoRidge

Polymer Nano-Umbilical

- $560,000 funding for 1 year research project funded 80% by RPSEA/DOE
  - Similar technology as NanoCable
- Carbon nanotube polymer based conductor for extended seafloor tieback power delivery
- Technip, Duco, Chevron, Rice University collaborators

NanoRidge

NMI Thermoplastics with CNT's

- Resistivity ≤ 10^5 Ω·cm achieved at ≤ 5 wt. % CNT in:
  - PEEK
  - PEKK
  - HDPE, MDPE
  - Polystyrene (PS)
  - Polyphenylene sulfide (PPS)
  - Polyurethane, polyurethane-methacrylate
- Resistivity of 10^0-10^1 Ω·cm achieved at ≤ 10 wt. % CNT in:
  - PEEK
  - HDPE, MDPE
  - Polyurethane-methacrylate
- Higher CNT loading reaches 10^{-1} Ω·cm in PEEK, HDPE

NanoRidge

Electrically Active Polymers

NanoRidge is currently seeking application targets within several conductivity ranges

- ESD (10^5 – 10^{12} Ω·cm)
  - Electronic components (e.g. anti-static housings)
  - Anti-static automotive parts
- EMI (10^0 – 10^4 Ω·cm)
  - This area is our primary focus
    - NanoCable is an enabling technology in this space
  - "Heatable" spray-on coating system
  - Advanced electronic components (e.g. wire and cable shielding)
  - Non-metallic protection (e.g. polymer Faraday cage)
  - Other areas of mutual interest
- Lightning strike protection (~10^{-3} Ω·cm)

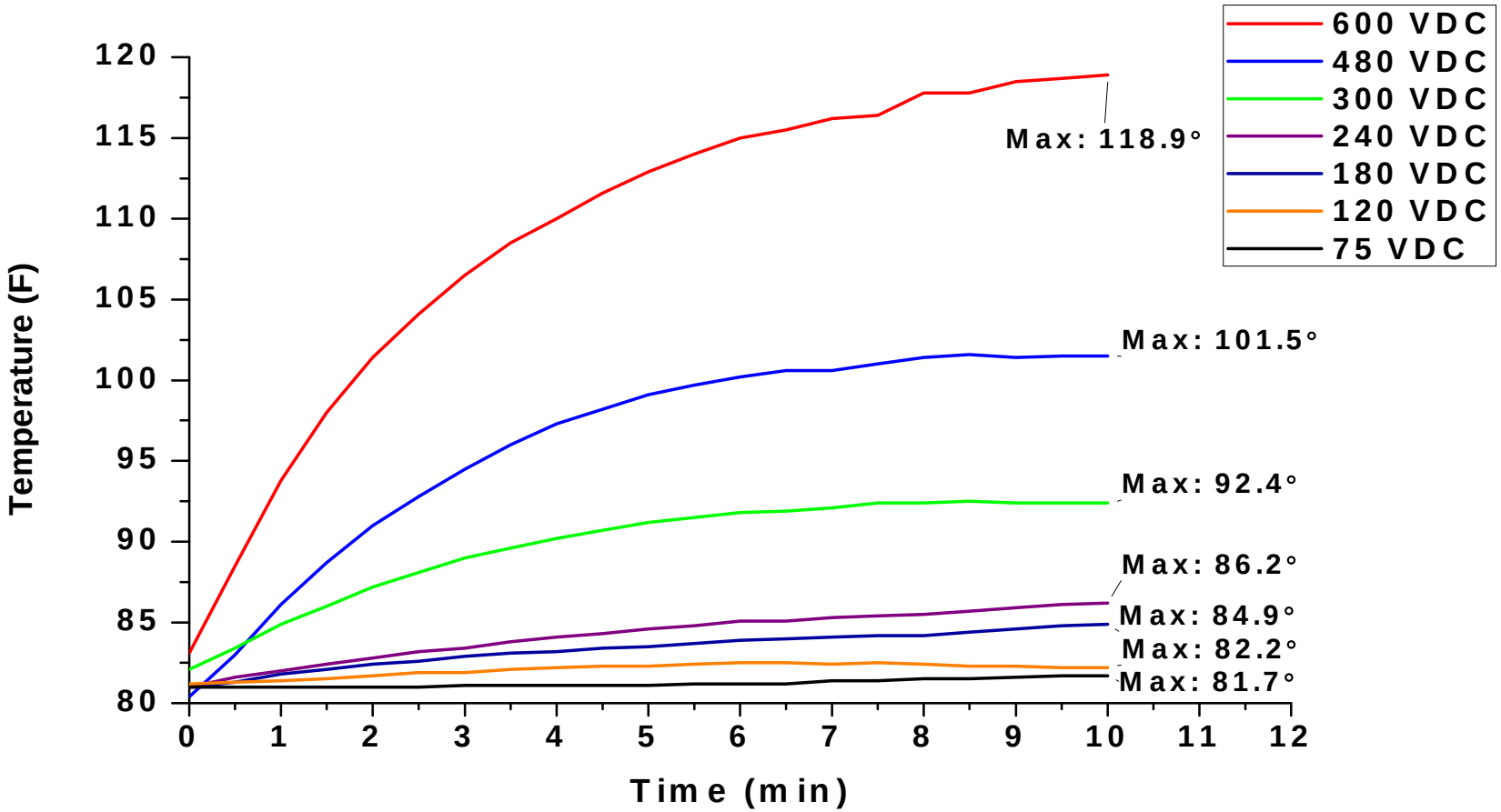
NanoRidge

Heatable Spray-on Coating System

- Base system is an “engineered” coating
  - Currently used for marine and anti-graffiti applications
- Characteristics include:
  - Moisture resistance
  - UV resistance
  - Acid/base resistance
  - Low permeability
  - Low surface energy
  - High durability
  - High flexibility
- Addition of nanotubes provides:
  - Resistive heating capability
  - Increased durability
- Primary applications include de-icing of airplane wing leading edges, wind turbine blades, and power towers
- Additional applications include oil & gas downhole applications

NanoRidge

Heating Performance of Coating System



Time vs. temperature curves of heatable coating at various applied DC voltages

NanoRidge

Heating Performance of Coating System

T= 0 min

T= 10 min

NanoRidge

Business Development

- Growth through partnering
  - Conductive coatings
  - Electrically active thermoplastics
  - Metals
- Key partner parameters sought
  - Current market leadership
  - Innovative approach to corporate business development strategies
  - Funding for product initiatives
  - Longer term outlook for optimal value creation, but shorter term application potential

NanoRidge

NanoRidge

NanoRidge Materials, Inc.
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Houston, TX 77023
713-928-6166

nanoUmbilical
Workshop

Ultra-High Conductivity Umbilicals

Enrique V. Barrera

Department of Mechanical Engineering and Materials Science, Rice University, Houston, TX 77005

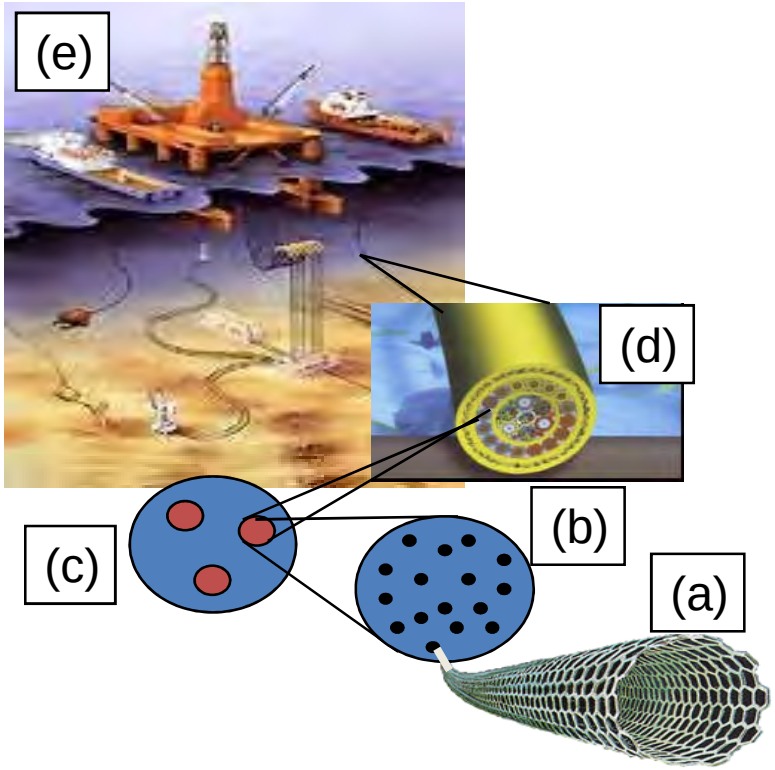
Outline

- Program Goals
- Background on Conduction via carbon nanotubes
- Program tasks and timeline
- Program team
- Outcomes

Program Goals: Reasons for Using SWNTs

Candidate Conductor	Material Availability	Degree of Electrical Conductivity	Processability	Costs	Time to Technology Maturation	Weight Saving Potential
SWNTs	Medium	High	High	High	3 years	High
MWCNT	Medium	Low	High	Medium	3 years	Medium
Nanowire	Low	Low	Med-High	High	5 Years	Low
Quantum Wire	Low	High	Low	High	10 years	High
Bucky Paper	Medium	Medium	Medium	High	3 years	Low

Program Goals: Polymer Nanotube Umbilical



The PNU is a polymer-nanotube wire that can carry high power to the sea floor.

(a) A SWNT as the conducting species for the conductor wiring.
(b) Cross-section of a Polymer Nanotube Umbilical (PNU) where nanotubes are dispersed in a polymer
(c) Cross-section for a three phase power cable,
(d) The umbilical cable that provides power lines to the seafloor, and
(e) The offshore platform and subsea system.

Nanotechnology: From the bottom up!

NanoRidge RICE UNIVERSITY Technip DUCO Chevron

Program Goals: Deliverables

(1) Bridge the gap between engineering science and manufacturing technology to produce a piece of wire.

The wire conductor will be a polymer-Nanotube composite that is half the diameter of a Cu conductor that can carry 500 amps at the same voltage used for the Cu conductor.

We will also produce the following:

(2) Report to RPSEA suitable for public release.

(3) A workshop to feature advances in power conductors for oil and gas use.

Program Goals: Umbilical Parameters

Overall objective is to:

- Design, build and test an engineering prototype of a working ultra-high conductivity “wire”.

- The wire could in later stages be incorporated into an umbilical exceeding 161 km (100 mile in length.

- It would be expected to deliver up to 10 MW at up to 36 kV.

- The operating envelop would range from -1 to 121ºC (~30 – 250ºF) and pressure from 0 to 31.03 MPa (0 – 4500 psi).

Program Goals: Conductor Size

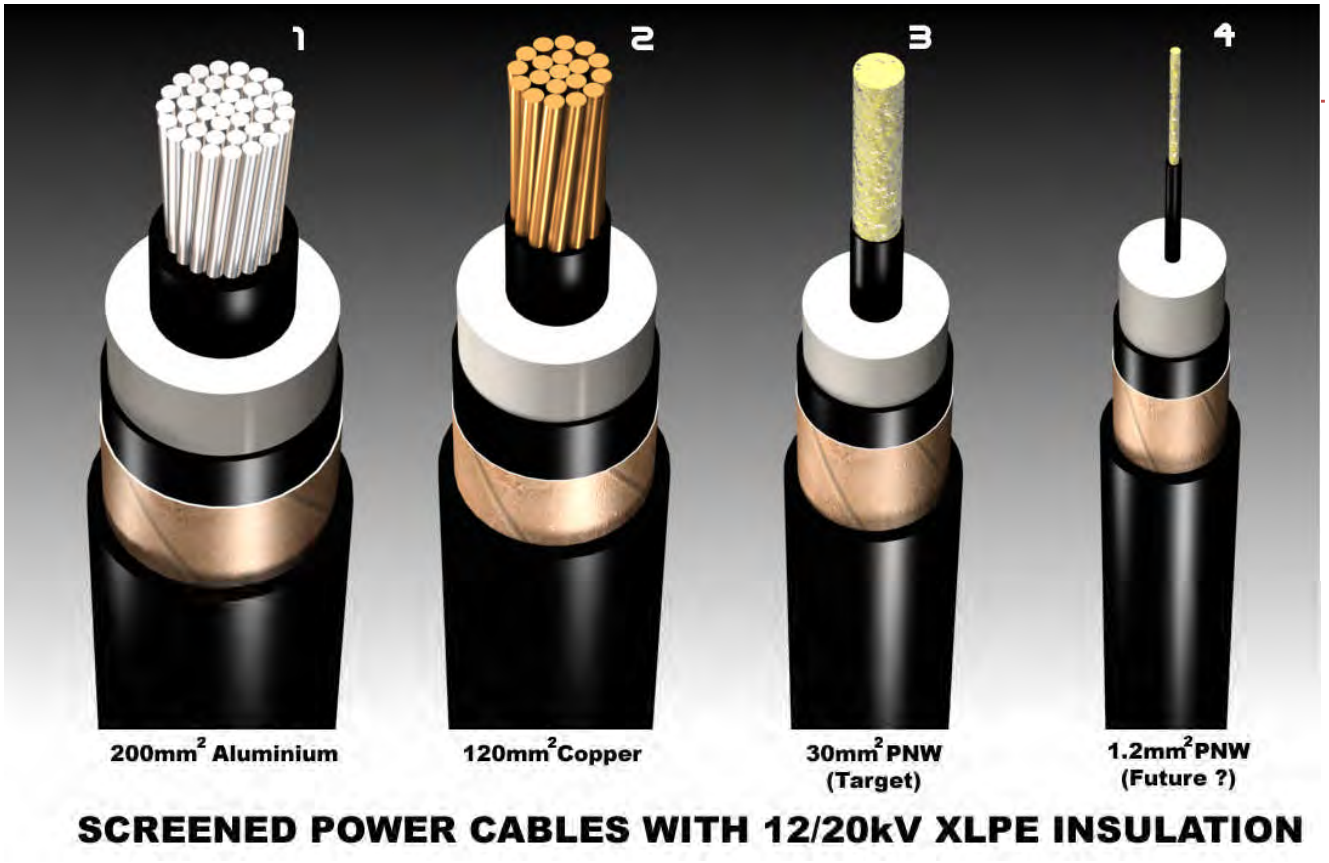


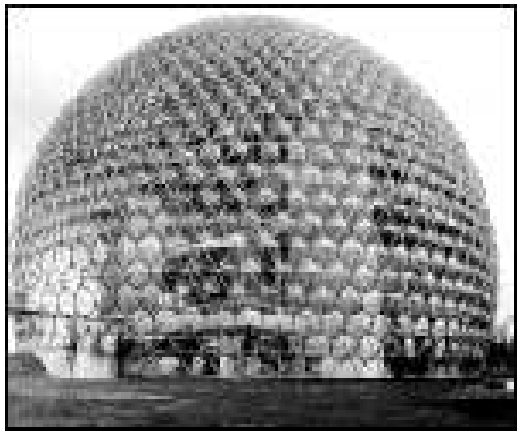
Table D.1.4.1	Cable 1	Cable 2	Cable 3	Cable 4
Cable (area) (mm^2)	200 (Al)	120 (Cu)	30 (PNU)	1.2 (PNU)
Mass in air (kg/m)	1.45	1.82	0.54	0.33
Diameter (m)	0.038	0.0327	0.0253	0.0195
Mass of displaced water (kg/m)	1.16	0.86	0.52	0.31
Weight in water (N/m)	2.820	9.406	0.242	0.234
Or (kg/m)	0.288	0.959	0.025	0.024

Picture compliments of Dave Madden

The Third Form of Carbon: Fullerenes

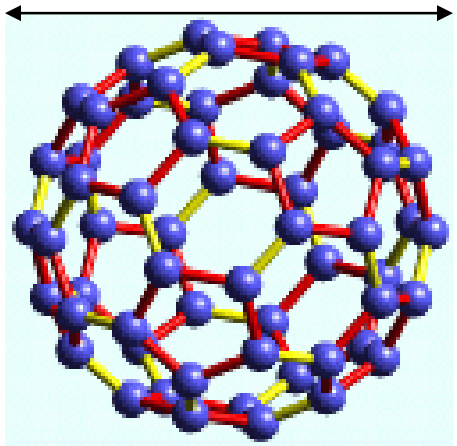
A soccer ball

Geodesic ball



Geodesic Dome

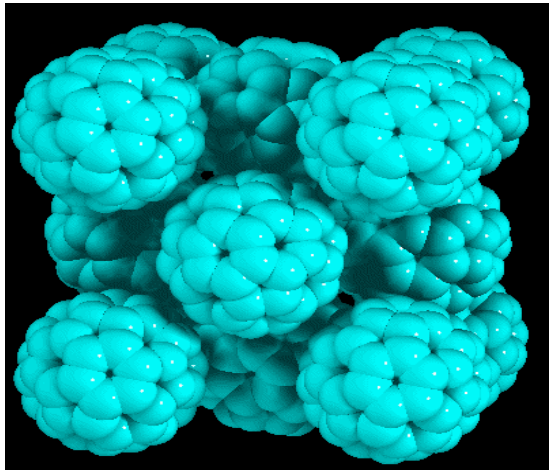
~ 10.14 A



C-C bond in C_{60}

When I am working on a problem,
I never think about beauty.
I think only of how to solve the problem.
But when I have finished,
if the solution is not beautiful,
I know it is wrong.

-------R. Buckminster Fuller

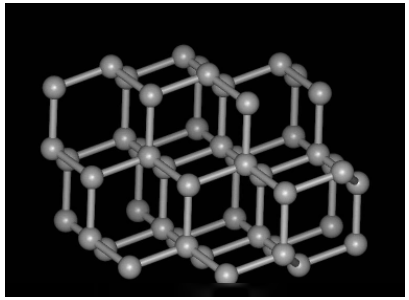


FCC solid C_{60}

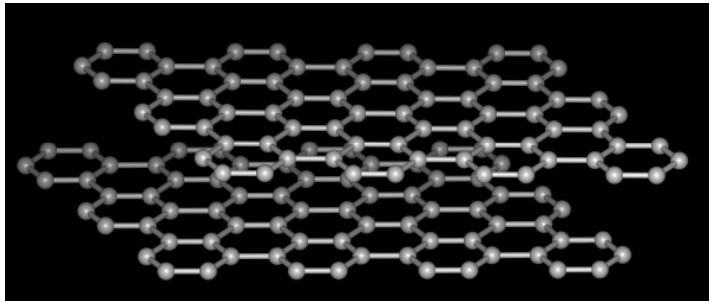
NanoRidge RICE UNIVERSITY Technip DUCO Chevron

Fullerenes and Nanotubes

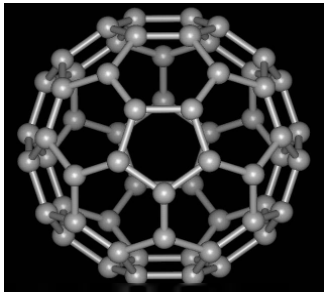
C60 was discovered in 1985.
Nanotubes were discovered in 1991.
Led to Nobel Prize in Chemistry in 1996.



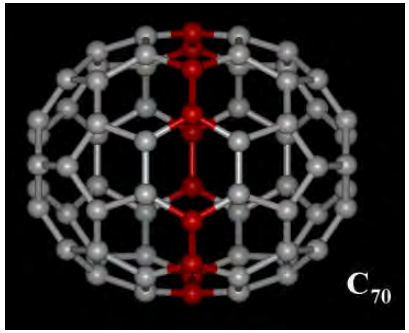
Diamond



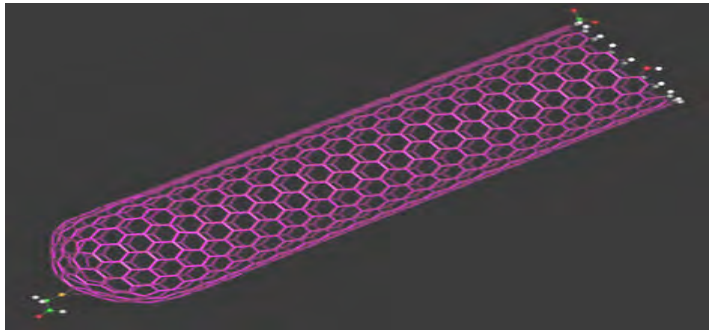
Graphite



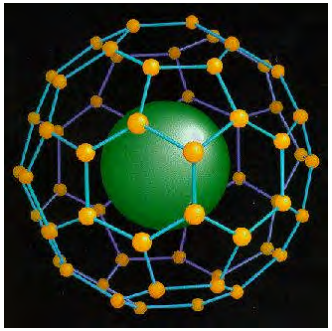
C_{60}



C_{70}

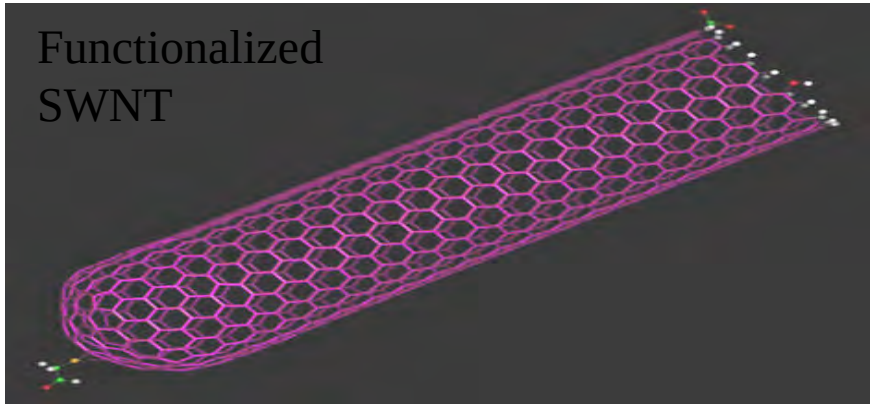


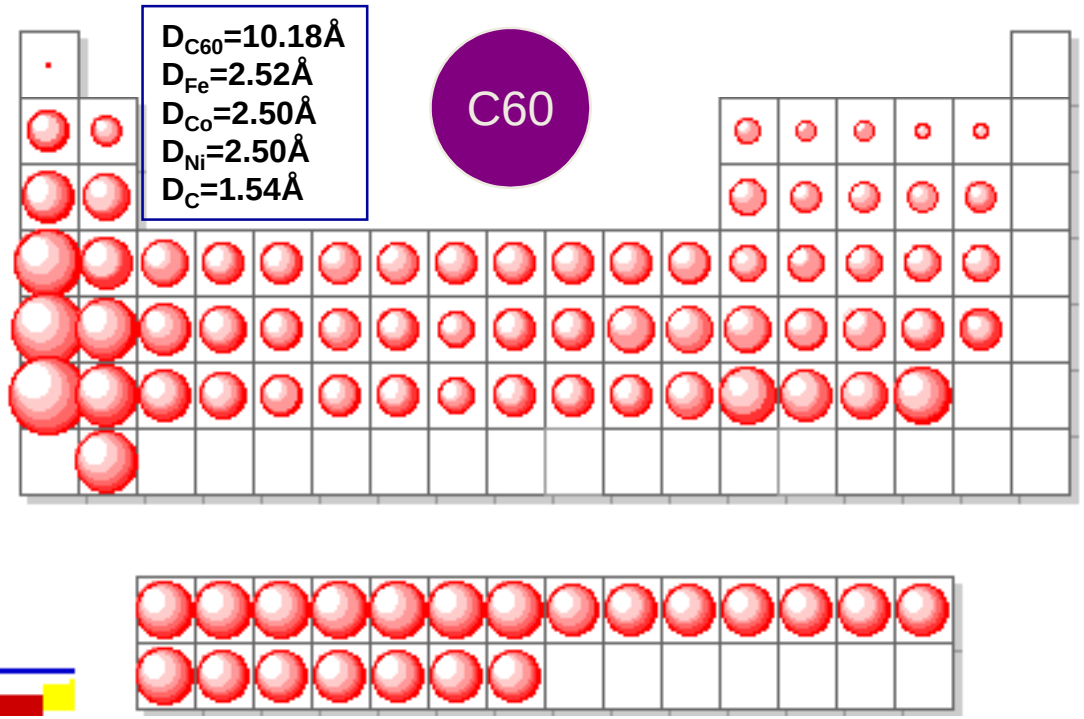
Nanotube

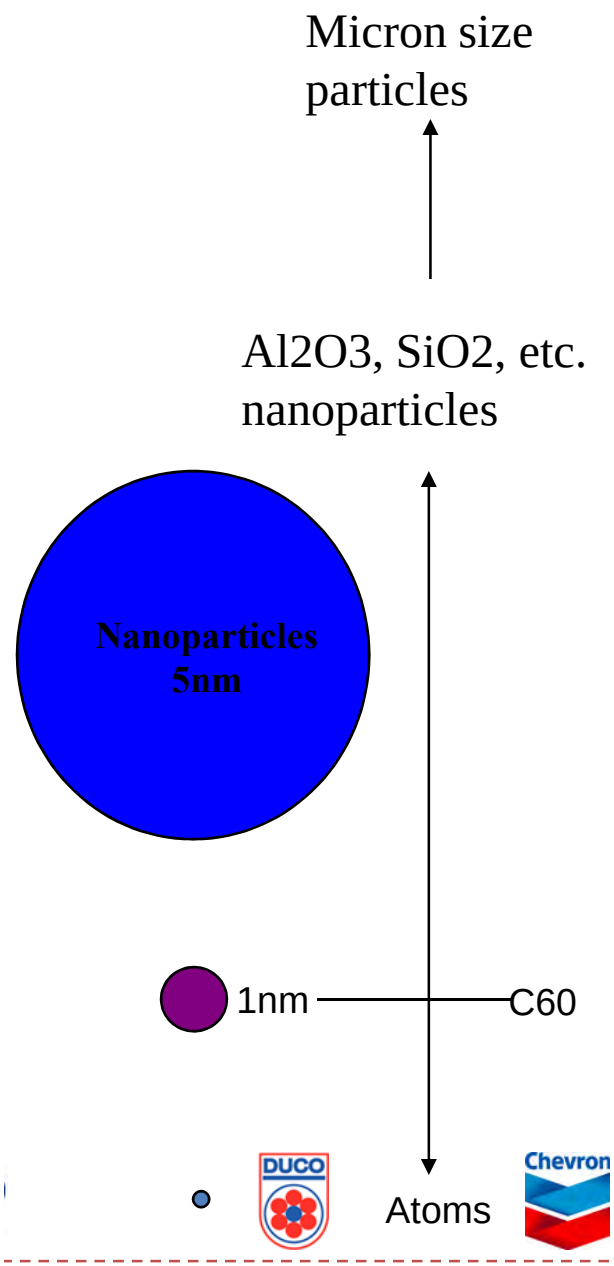


Endohedral C_{60}

Size Comparison of Single C_{60} , Nanotube to Basic Elemental Atoms and Nanoparticles







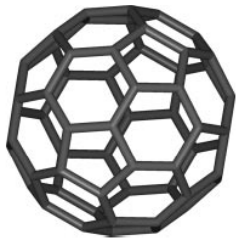
Nanotubes: Data Sheet Engineer's Perspective: Broad Property Range

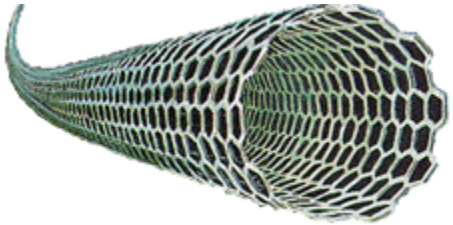
Fullerenes (C_{60})

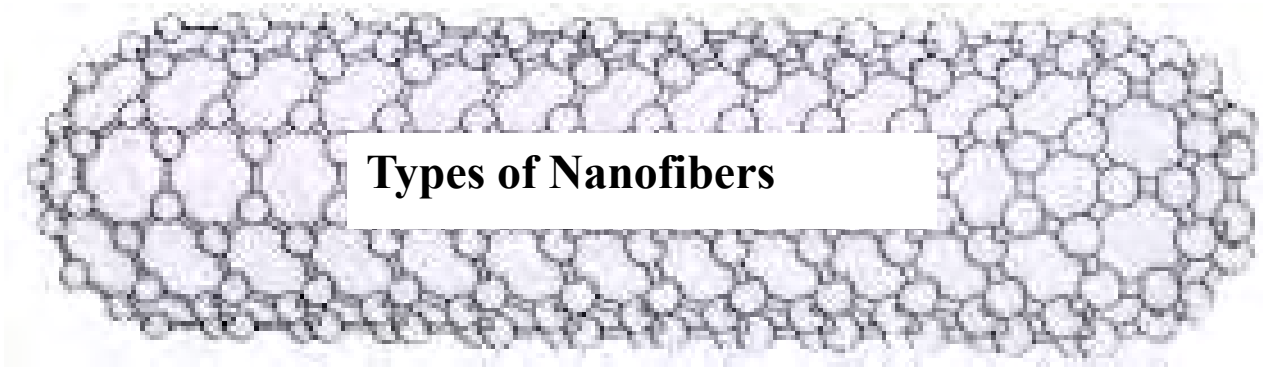
- **Low thermal conductivity** (0.4 W/m•K)
- **Point scatterer** (~ 1 nm spherical particle)
- **Grain boundary and interfacial effects**

Single Walled Carbon Nanotubes

- Dimensions: 1nm (dia.), 0.3 – 100 μm (length)
- Density: 0.89g/cm^3
- Tensile strength ~50GPa
- Tensile Modulus ~1TPa
- Elongation to failure ~5%
- Electrical Conductivity ~1800-2000 ohms^{-1}
  Semiconducting to conducting like copper
- Thermal conductivity (C_{60}) low in
  transverse direction and high (diamond)
  along tube axis (~2500 W/m•K)
- Nanoscale scattering defects
  - Tubes intact or removed in situ (nanovoids)
- Bonding by van der Waals or by functionalization







Types of Nanofibers

End capped single wall nanotube

Which nanofibers/nanotubes are of significance to future nanocomposite materials?

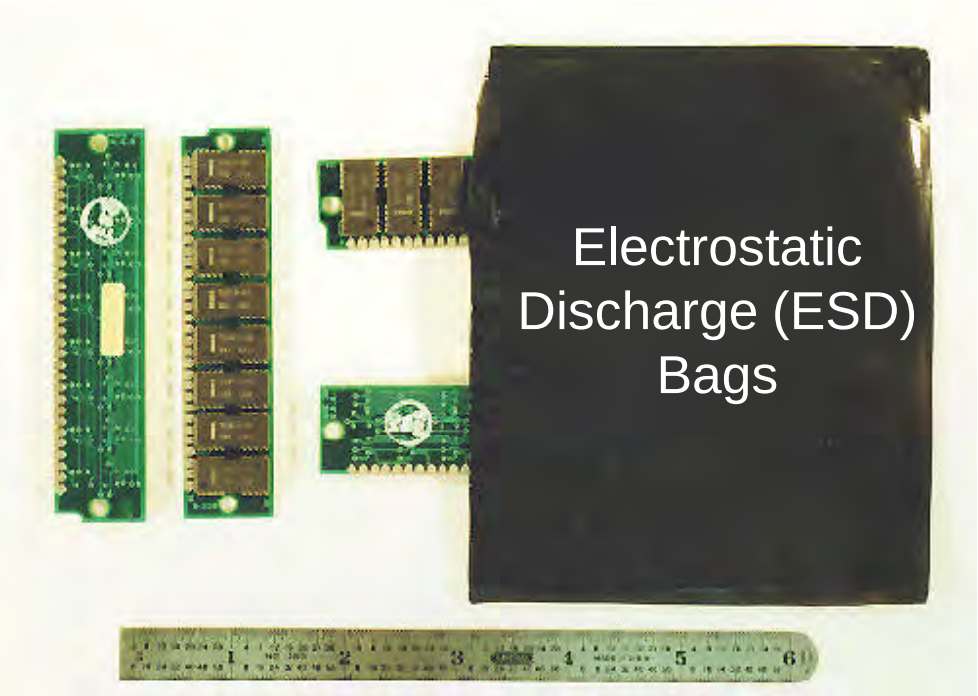
Carbon Fibers:	Type III	Type II	Type I
Nanofibers:	VGCFs	MWNTs	SWNTs
	Useful $0.10/g	Moderate ~$50/g	High Strength & Modulus $500/g (as low as $1/gram)

VGCFs have defects and have large diameters (100 nm)
MWNTs are defected and not as optimal in some cases.
SWNTs are the Holy Grail! No defects, high strength and stiffness.
All have useful anisotropic thermal and electrical properties.

Background on Conduction: Polymer Nanotube Conductors: Pathway to a High Conductor

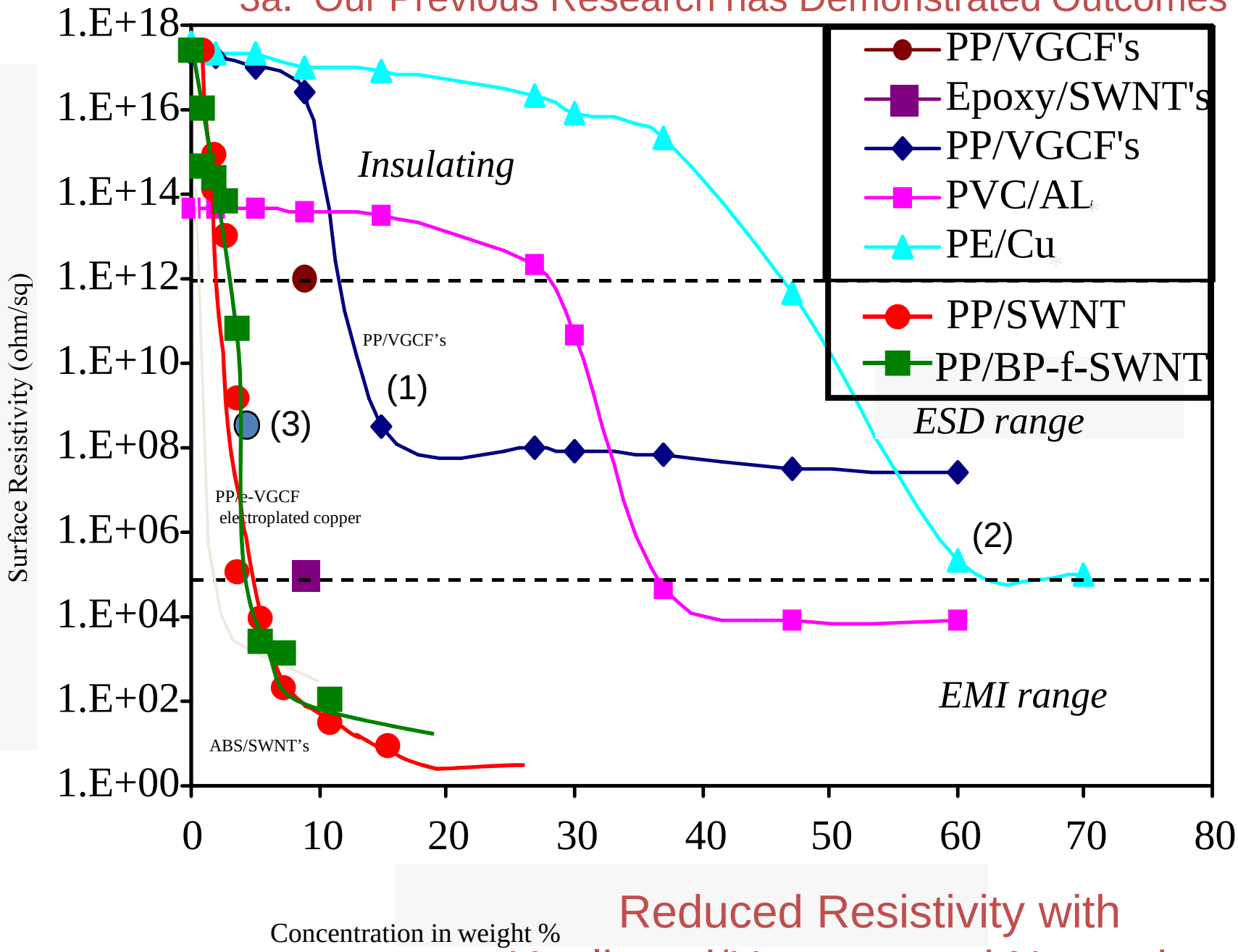
1996-1999: 13 to 14 orders of decrease in electrical resistivity.
1997-1999: Produced Electrostatic Discharge (ESD) materials.
2000: Produce multifunctional Nanotube Continuous Fibers (NCFs).
2002: Produced Electromagnetic Interference (EMI) Materials.
2005: Produced conducting wire.
2007: Produced Lightning strike protection.
2009: First Polymer Nanotube Umbilical (1 ft *Demonstration Sample*).

2009: 19 orders of magnitude decrease in electrical resistivity.



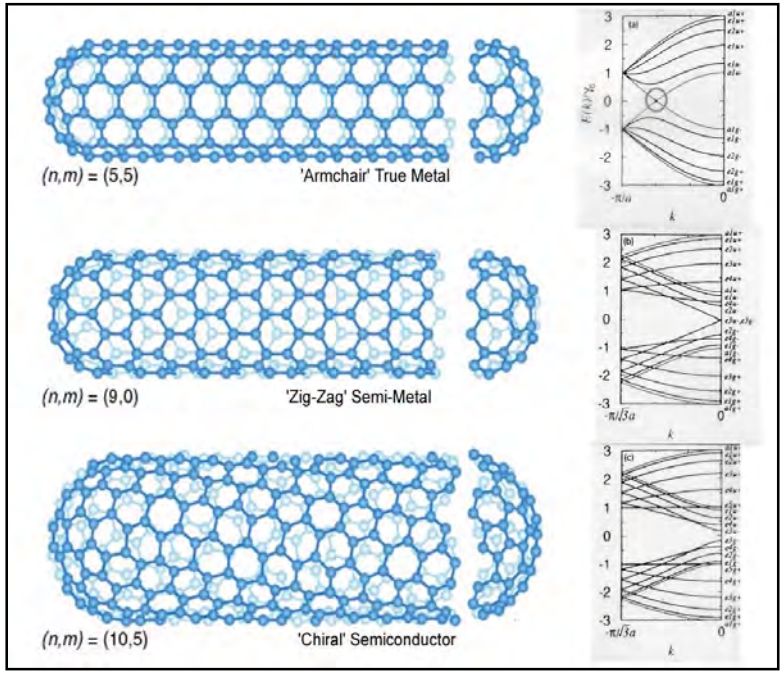
Demonstration Sample in 1999 showing an ESD bag that will hold computer parts. Bag showed rapid discharge in a range of relative humidities.

3a. Our Previous Research has Demonstrated Outcomes



Reduced Resistivity with Unaligned/Unseparated Nanotubes

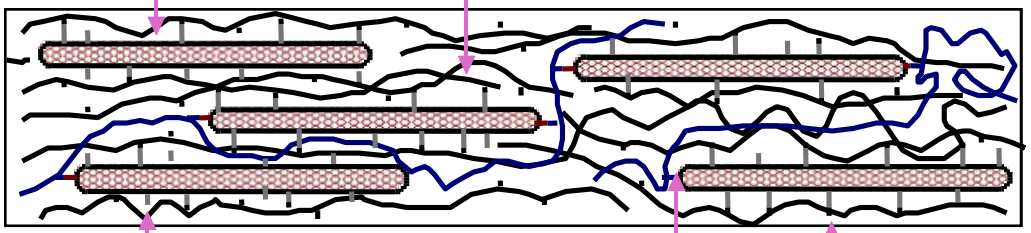
Background: Nanotechnology Basis for the PNU



Fully Integrated Nanotube Composites to Achieve Cold Forming

Align single nanotubes by shear/elongational processing.

Remove excess and unwanted matrix.



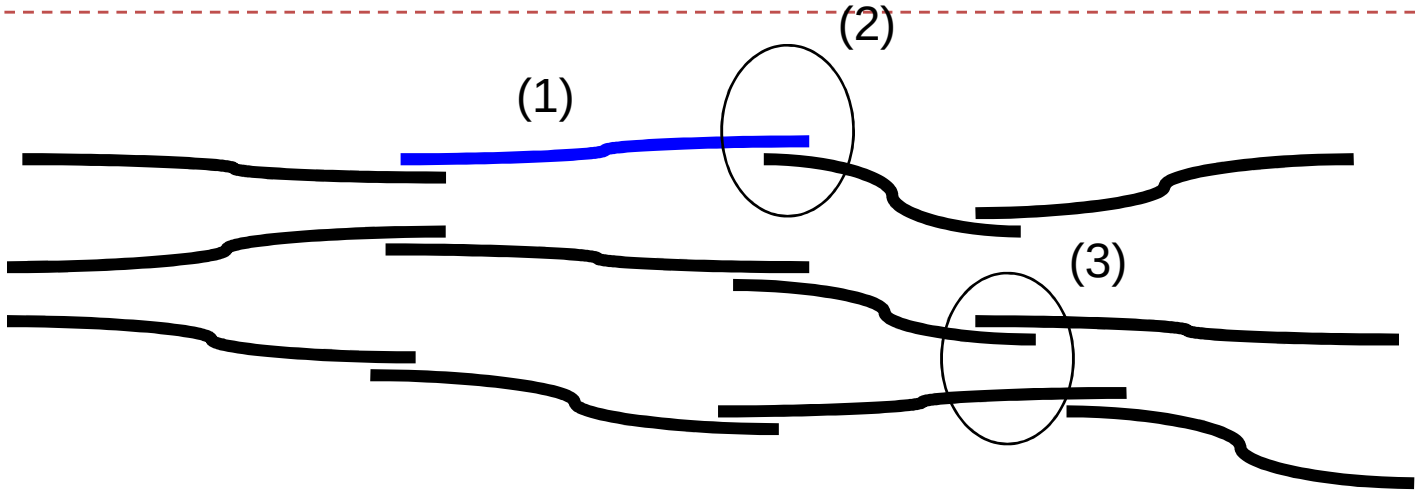
Functionalize (i.e., polymerize) to fully integrate.

Identify appropriate functionalization: Side wall vs. end attachment.

Of the dozens of known nanotube types, one third are metallic; the rest are direct band-gap semiconductors. The metals, especially the 'armchair' tubes, have been shown to conduct electricity at least as well as copper, and perhaps some ten times better.

A PNU consist of aligned SWNTs in a polymer matrix such that misalignment assures electrical contact while providing for robust mechanical strength. Use of metallic SWNTs ensures high electrical conduction. Optimizing the concentration of the SWNTs ensures costs control and near term use.

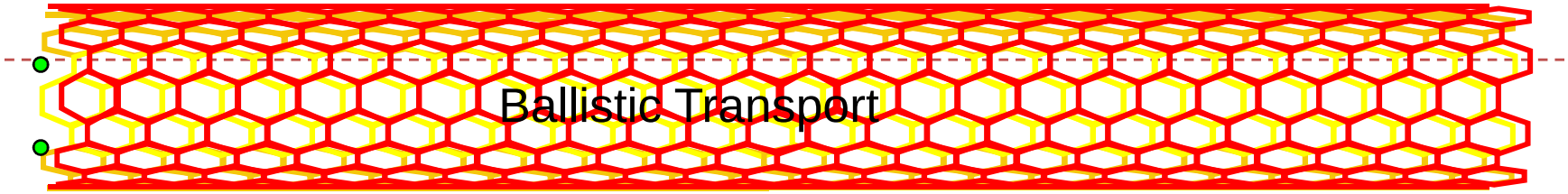
Background: Directed Nanotube Network (DNN)



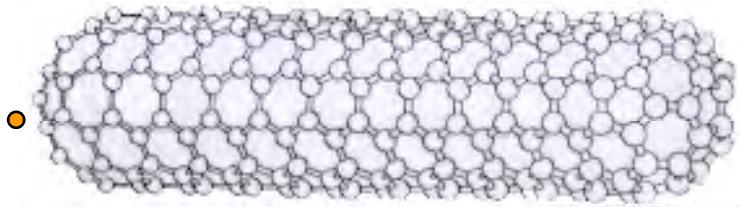
A schematic depicting a network of (1) m-SWCNTs that are arranged to promote maximum electrical conduction. The network is made up of (2) connected nanotubes that provide for *ballistic transport* along the nanotube length and *resonant quantum tunneling* from one nanotube to the other. Gap distances between the various chains prevent electron hopping from one pathway to the next. m-SWCNTs may vary in length but the (3) connections will be optimized for low contact resistance.

Nanotubes are nanometers (1.4nm) in diameter and microns in length.
Electrical conduction is as high or better than copper.
Mechanical properties include: UTS: ~50-150GPa/Elastic Modulus: 1 TPa

Background: Electron Transport Mechanisms

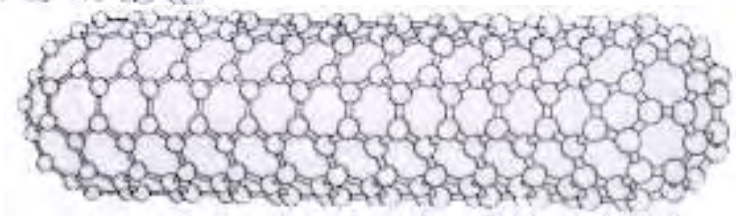


Ballistic conduction allows electrons to flow through the material without collisions. The collisions cause the electrons to slow down, and cause the material to heat, effectively creating resistance in the material.



Transport

Hopping



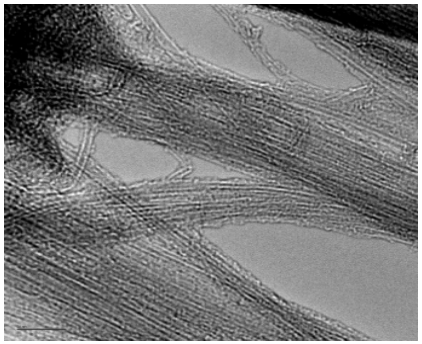
Hopping conduction allows electrons to jump from one nanotube to another. Short contact lengths limit electrons from jumping back and forth.

To maximize conduction, Metallic Nanotubes are needed.

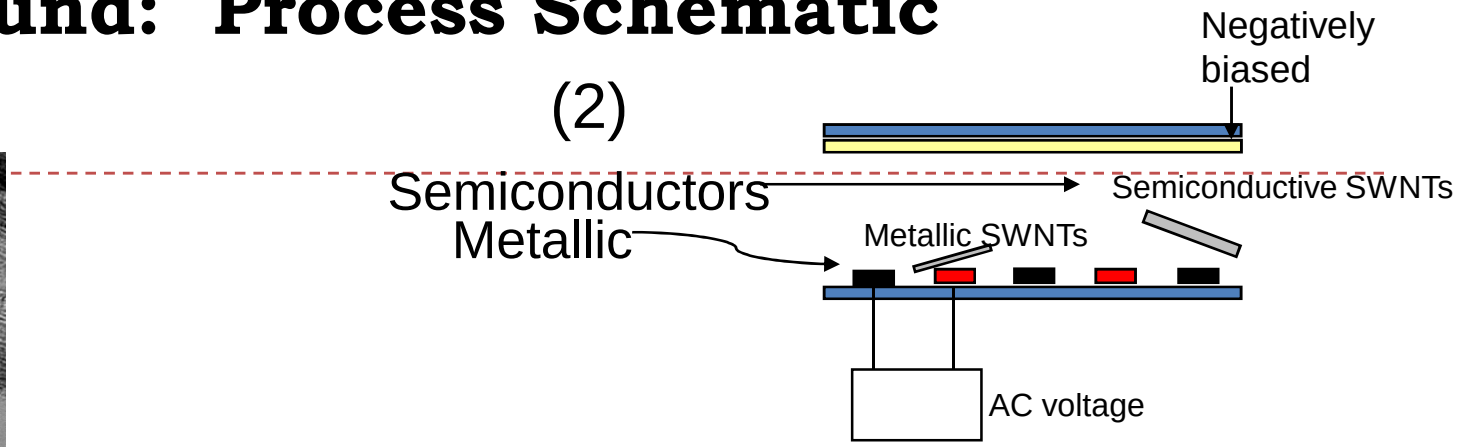
Alper Buldum and Jian Ping Lu, Phys. Rev. B 63, 161403 R (2001).

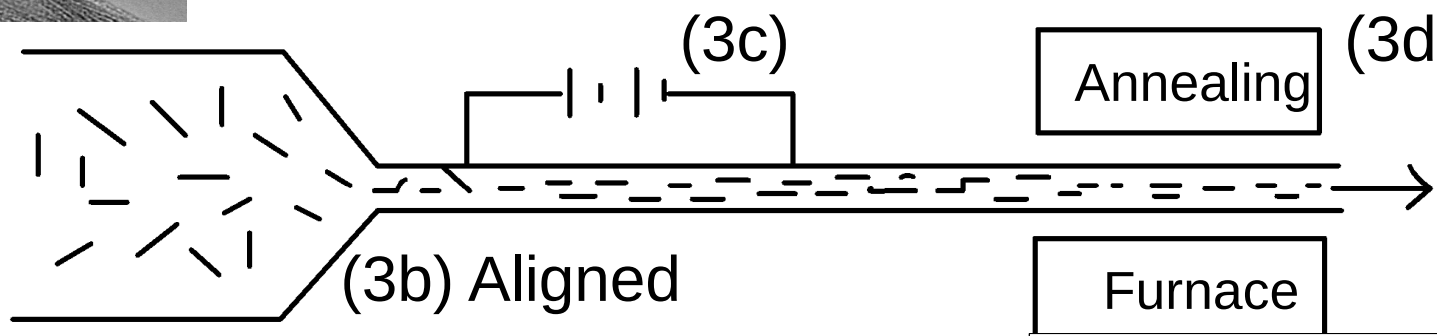
Background: Process Schematic

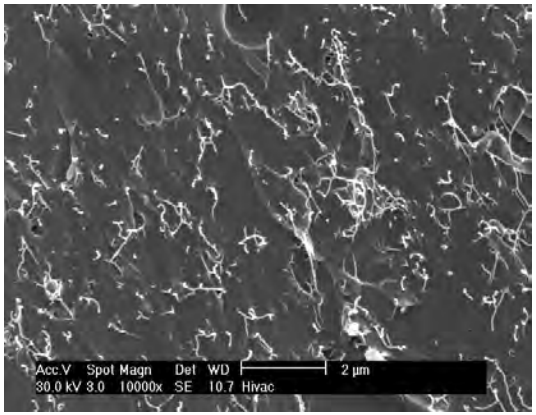
(1)

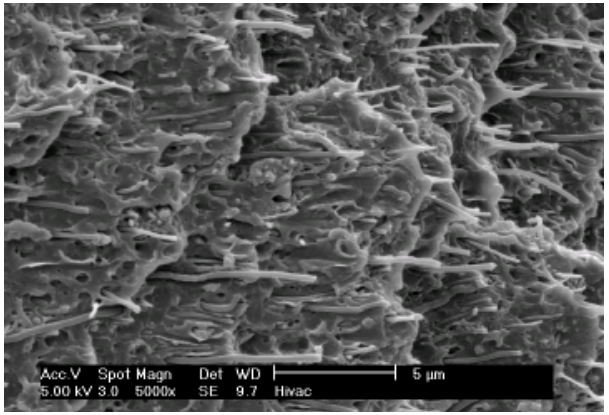


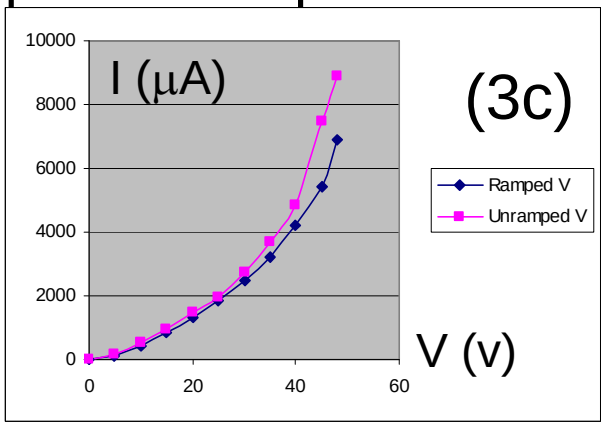
(2)











Tasks and Goals for the PNU Program

Technical Tasks (Monthly)	J	F	M	A	M	J	J	A	S	O	N	D
a. Obtain SWNTs & m-SWCNTs	a	a	a	d	d							
b. Process wires w/polymer 1 & 2	b	b	b	c								
c. Test properties of 1 & 2 wire		c	c	c								
d. Characterize m-SWNTs		d	d	d	d							
e. Conduct NT-NT study		e	e	e	e	e	f	f	f			
f. Improve NT-NT conduction		f	f	f	f	f	f	f	f			
g. Disperse SWNTs in 1 & 2	g	g	g	g								
h. Disperse m-SWNTs in 1 & 2			h	h	h	h	h	h	h	h		
i. Implement Electric Fields				i	i	i	i	i	i	i	i	
j. Characterize NT filled wires				j	j	j	j	j	j	j	j	j
k. Conduct physical tests				k	k	k	k	k	k	k	k	k
l. Connection study	l	l	l	l	l	l	l	l	l	l	l	l
m. Reporting			m			m			m			m
Milestones	**J**	**F**	**M**	**A**	**M**	**J**	**J**	**A**	**S**	**O**	**N**	**D**
1. Obtain m-SWCNTs			X									
2. Produce first 1 ft wire						X						
3. Evaluate for umbilical									X			
4. Evaluation & optimization									X			
5. Optimize and prototype test												X
6. Final Report												X
7. nano-Umbilicals Workshop												X

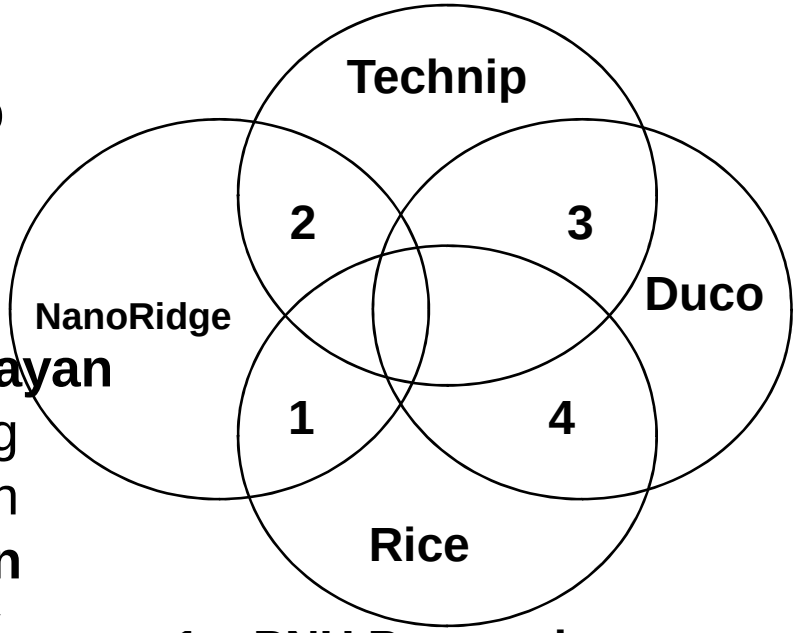
NanoRidge RICE UNIVERSITY Technip DUCO Chevron

Status of Tasks and Goals as of December 10, 2009

Technical Tasks (Monthly)	Completion Date	Status
a. Obtain SWNTs & m-SWCNTs	May	Completed
b. Process wires w/polymer 1 & 2	April	Completed
c. Test properties of 1 & 2 wire	April	Completed
d. Characterize m-SWNTs	May	Completed
e. Conduct NT-NT study	September	In progress
f. Improve NT-NT conduction	September	Completed
g. Disperse SWNTs in 1 & 2	April	Completed
h. Disperse m-SWNTs in 1 & 2	October	Completed
i. Implement Electric Fields	November	Completed
j. Characterize NT filled wires	December	Completed
k. Conduct physical tests	December	In progress
l. Connection study	December	Completed
m. Reporting	Monthly	Completed
Milestones		
1. Obtain m-SWCNTs	March	Completed
2. Produce first 1 ft wire	June	Completed
3. Evaluate for umbilical	September	Completed
4. Evaluation & optimization	September	Completed
5. Optimize and prototype test	December	In progress
6. Final Report	December	Pending
7. nano-Umbilicals Workshop	December	In Progress

Program Team

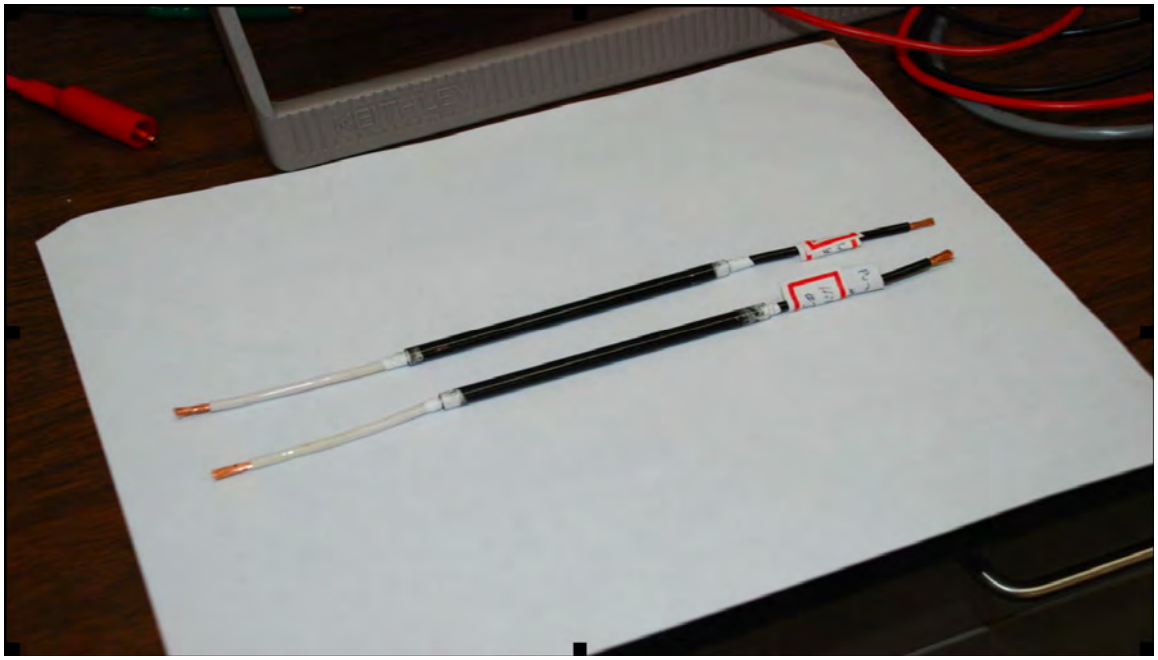
NanoRidge Materials, Inc.
Program Lead Organization
Dean Hulsey, Lori Jacob
A nanotechnology company specializing in research to engineering applications"
Rice University
Enrique Barrera, Pulickel Ajayan
Highly recognized institution for conducting carbon nanotube nanotechnology research
Technip, USA **Jim Dailey, Kerri Dawson**
An engineering and construction company in the oil and gas services sector
DUCO, Inc. **Dave Madden**
An umbilical designer, manufacturer and supplier for the oil and gas industry



1 – PNU Processing
2 – Process Specification
3 – Umbilical Specification
4 – Connector Study

Outcomes: Polymer Nanotube Umbilical

A PNU Test sample configuration where a number of the processing conditions are used.



Processing Tasks

h: Dispersion

i: Electric Fields

b: Annealing

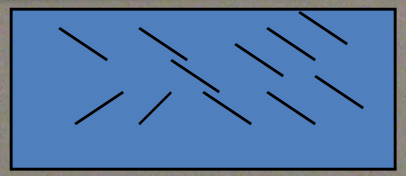
A Dymex polymer (thermoset) is shown here.

A method to produce the test sample to a one foot length has been identified and is currently being considered (Proprietary).

Outcomes: Produce 1st One Foot Wire

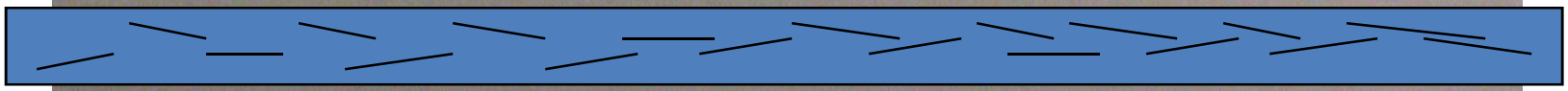
PE w/10 wt% SWNTs/Processed by melt spinning.
Various diameters have been produced with smaller diameters being more optimal at this time.

A PNU wire is shown below which exceeds one foot in length.
A number of the processing tasks were used: a, b, f, g, h, i, and l.



Explanation for thinner wire, better conductivity

Keep the same volume, 1/2 diameter, ¼ cross section area, 4 x length



Better alignment in uniaxial direction

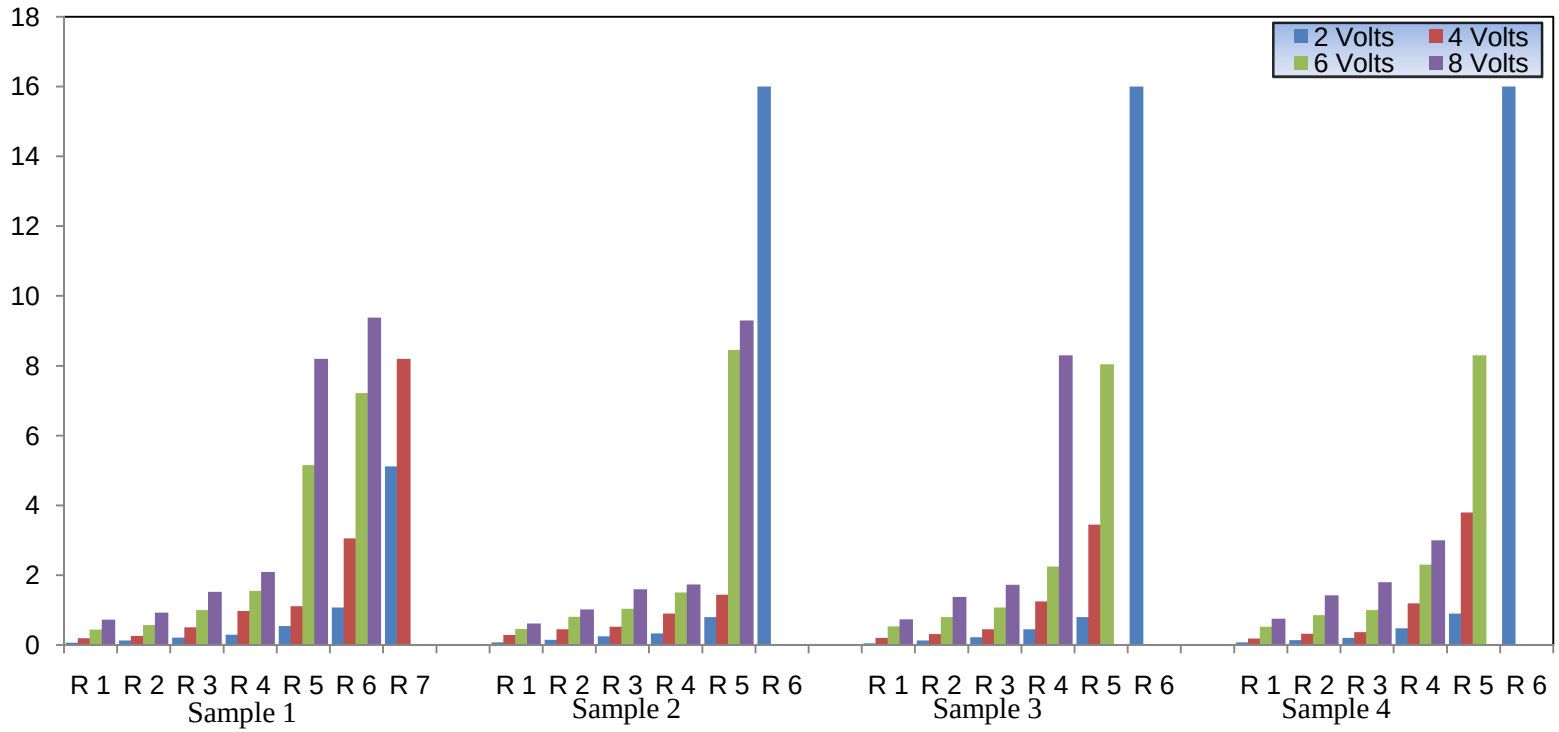
Samples for Resistivity Testing

Sample	Resistivity (ohm.cm)	Diameter (cm)	X-section area (cm^2)
Polyethylene (HDPE)	10^{17}	0.394 (~0.4)	0.12
10 wt% CG / MDPE	~ $1* 10^3$ – $1.5* 10^3$	0.394	0.12
10 wt% CG / MDPE (application of electric field) at room temperature.	~ $5 * 10^{-1}$ – 10	0.394	0.12
10 wt% purified Hipco / MDPE (application of electric field) at room temperature.	~ $2 * 10^{-1}$ – 5	0.394	0.12
10 wt% CG / MDPE (application of electric field) at high temperatures)	~ $4*10^{-2}$ – $6*10^{-2}$	0.394	0.12
10 wt% purified Hipco / MDPE (application of electric field) at high temperature.	~ $2*10^{-2}$ – $6*10^{-2}$	0.394	0.12

Sample	Resistivity	Diameter	X-section area
10 wt% p-Hipco, w/ single core lead	~ $7*10^{-2}$ - $9*10^{-2}$	0.394	0.12
10 wt% p-Hipco w/ smaller diameter	~ $4.5*10^{-1}$ - $8*10^{-1}$	0.2	0.03

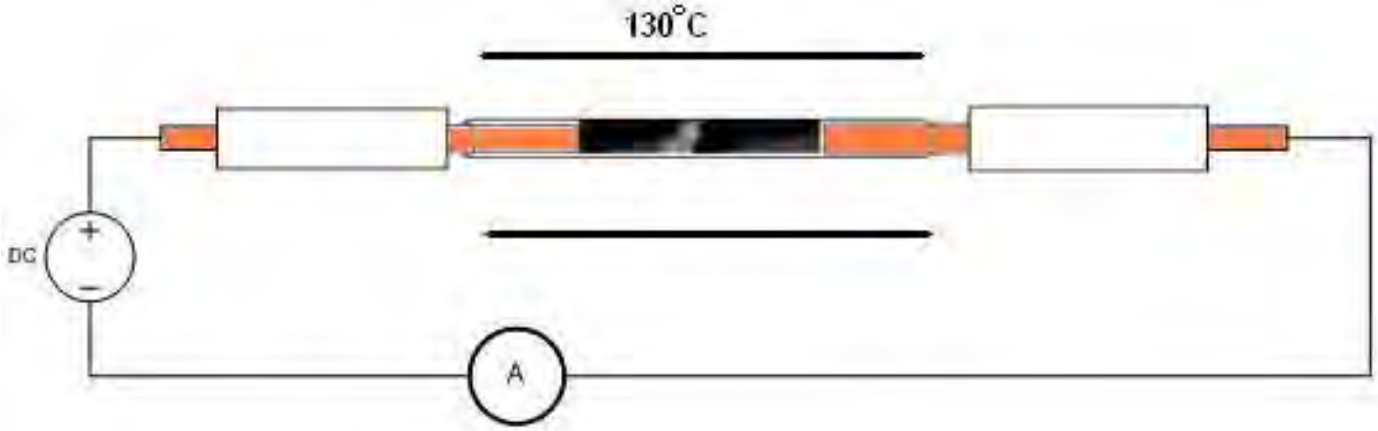
Current Study: Evaluation & Optimization

Target: 500 amps at the same voltage for the copper conductor.
Proposed: (a) Stranded wire (19 strands) or (b) Solid Core wire.
For stranded wire: On average ~26 amps to be carried by each strand.
Current Design and Evaluation: Single strand of SWNTs/PE.



Recent conditions may be limited by available power supply.

Current method for implementing the electric field

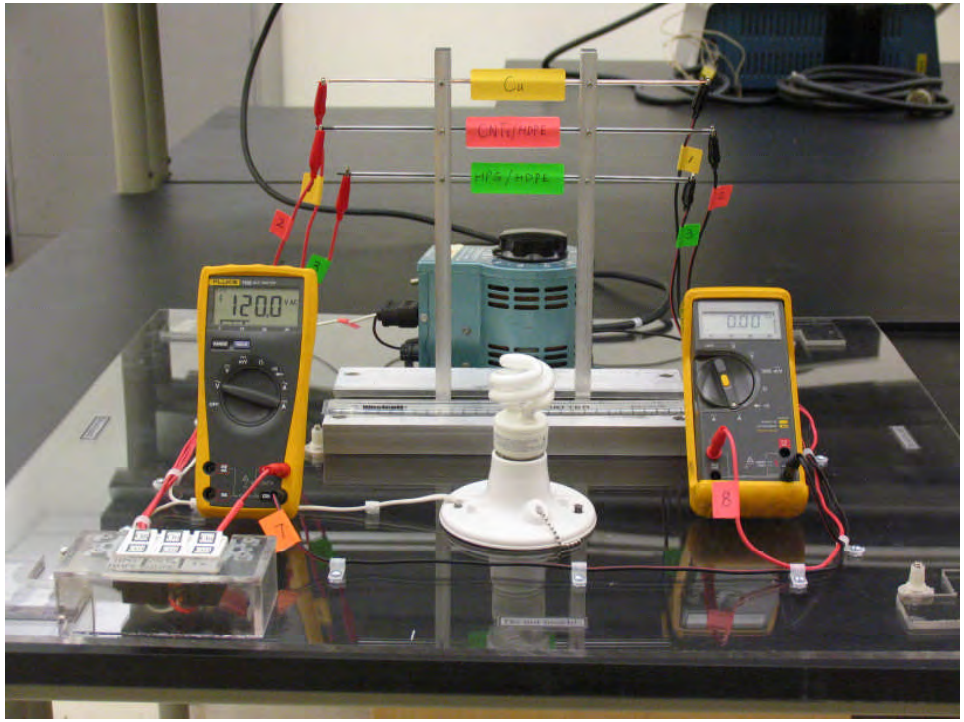


- 4 samples (MDPE + 10 wt% SWNTs) were tested.
- Samples required 4 ~ 5 rounds of conditioning, before it starts conducting well.
- Conditioning rounds were reduced with improvements made to the test sample.

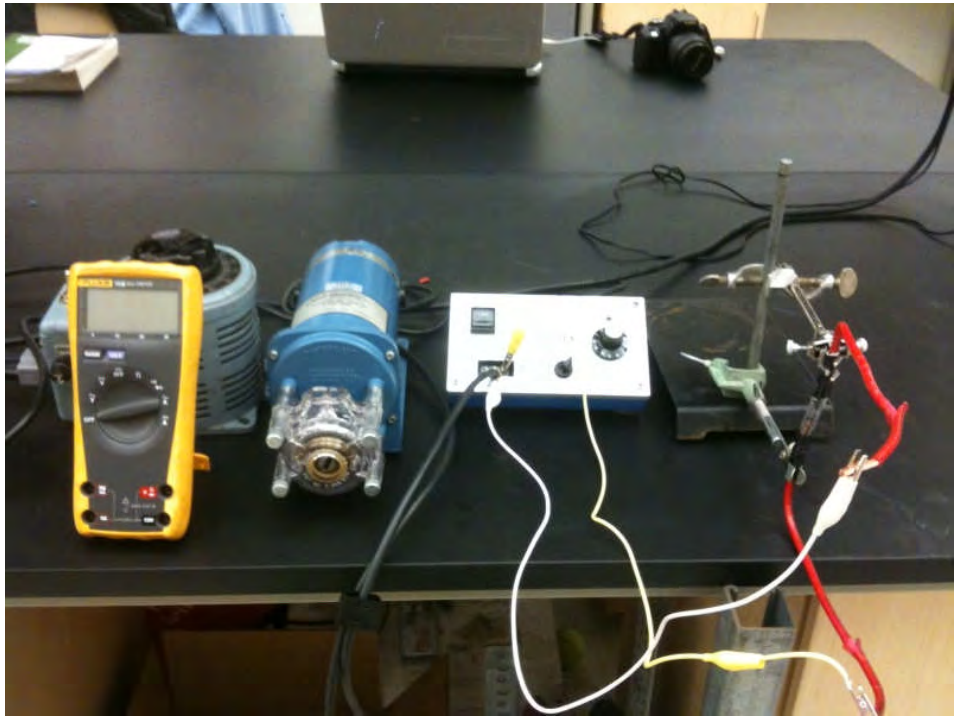
- The best samples carried a current of close to 16 amps for 2 V.
- The distance between the leads for the best sample is close to 0.7-7.62 cm.
- Specific resistivity was 2.1 * 10^{-2} ohms / sq cm

Outcomes: Demonstrations

Two demonstration set-ups to show samples produced and conditions tested.



Set-up #1: Demonstration with a light Bulb. Comparisons.



Set-up #2: Demonstration with a Pump. Higher voltage condition.

Outcomes: What was Learned

Partial listing related to conduction (with a low concentration focus):

- Approach: Advance materials properties by adding nanotubes then **lower** concentrations to get even more advancements.
- Dispersing nanotubes in the polymer leads to conduction at **low** concentrations while segragated nanotubes in polymer do not enhance mechanical strength.
- Nanotubes dispersed in a polymer fiber enable handling aligned nanotubes for a range of applications at 0 to 100% concentrations.
- Synergism between various nanoconstituents leads to enhancements at **lower** concentrations than used by the individual additives.
- Nanotubes can act as templates for other nanoconstituents to promote multifunctionality at **low** concentrations.
- A Directed Nanotube Network (DNN) can produce high conduction while **low** concentrations of nanotubes can be used.

Outcomes: Talking Points

- Produced PNUs with nanotube concentrations up to 90 wt%.
- Polyethylene, Dyamx, and polystyrene were used as the polymers.
- The lowest resistivity value reached was $2*10^{-2}$ Ωcm.
- The highest voltage carried by the PNU was 40V (the limit has not been evaluated).
- The highest current carried by the PNU was 16 A (not fully optimized).
- Several new steps for lowering the resistivity have been identified.)

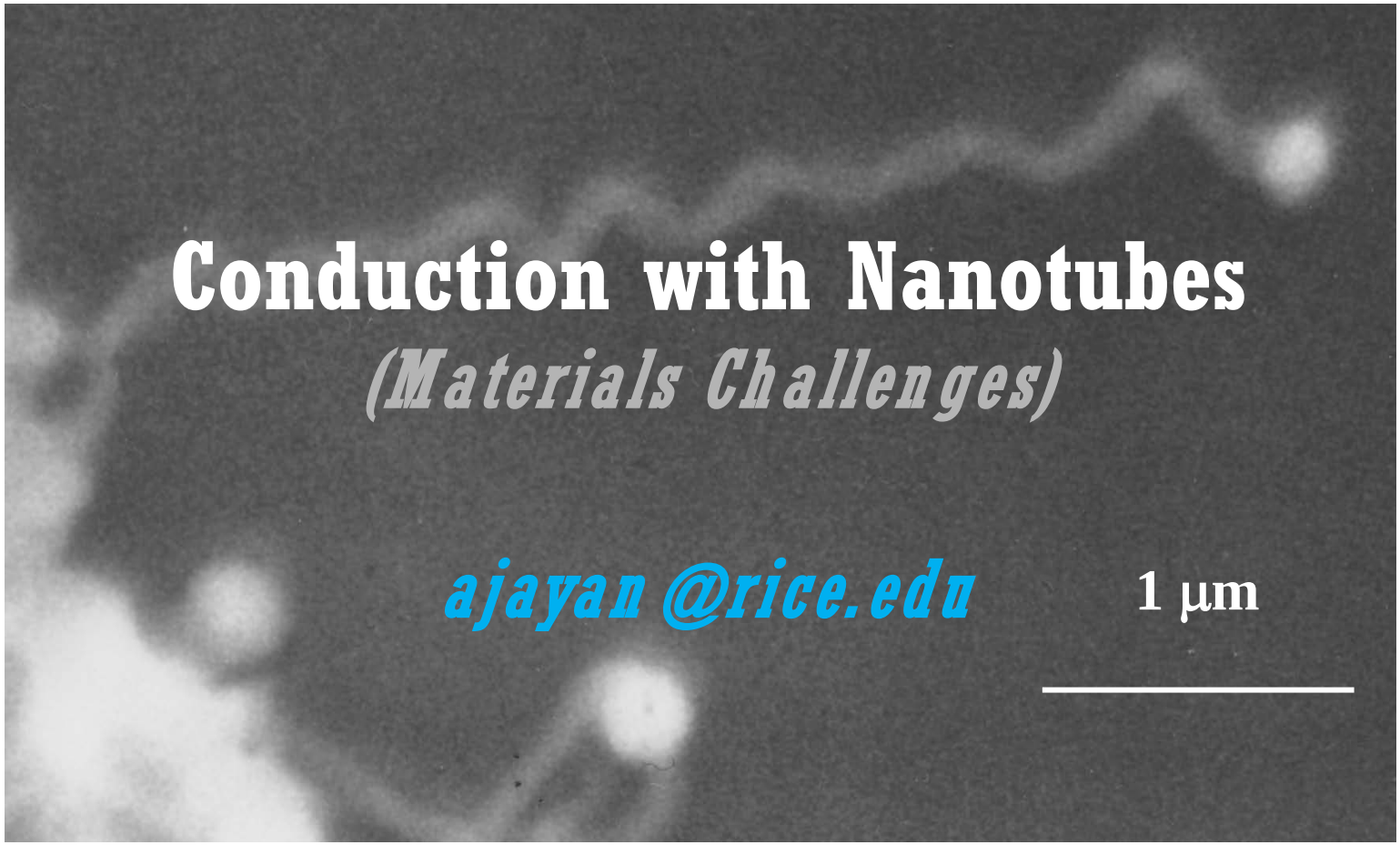
Outcomes: Supplemental Enhancements

- Enhanced purification
- Microwave heating (proprietary)
- Centrifugation
- Functionalization
- Annealing
- Higher concentrations
- Doping
- Enhanced NT-NT connections
- Retained polymer
- Stretching

Conduction with Nanotubes

(Materials Challenges)

ajayan@rice.edu



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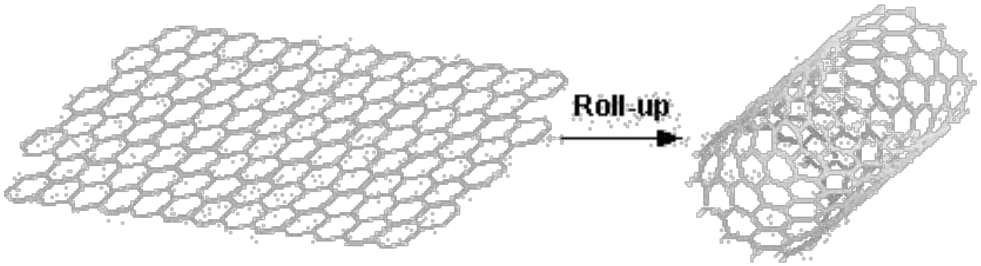
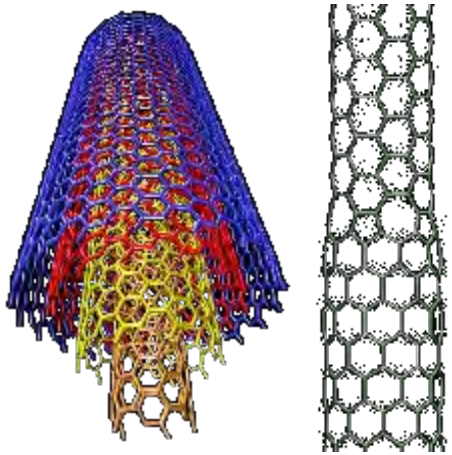
Alternate Conductors for the Future: Carbon?

Carbon nanotube (CNT):
- a scroll of a graphene sheet
- single (SWNT) or multiwalled (MWNT)



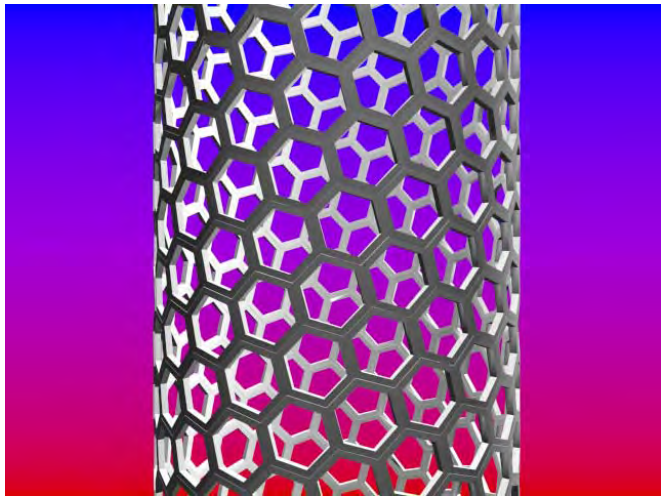


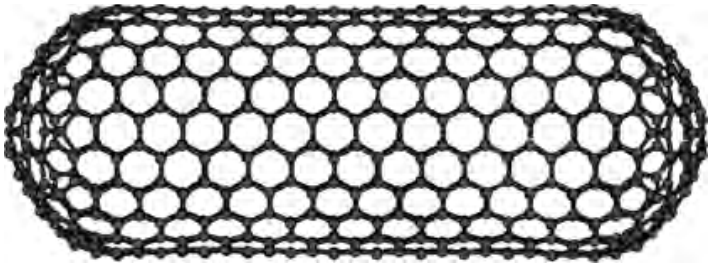
Electrical conductivity:	**metallic or semiconducting**
Energy gap:	**Eg [eV] ≈ 1/d [nm]**
Electrical transport: ballistic, no scattering	
Max. current density:	**10^{10} A/cm^2**
Diameter:	**1-25 nm**
Length:	**up to mm**
Thermal conductivity:	**6000 W/(Km)**

Electrical transport, thermal conductivity and current carrying capacity make CNT an ideal candidate for conducting wires

RICE

Carbon Nanotubes

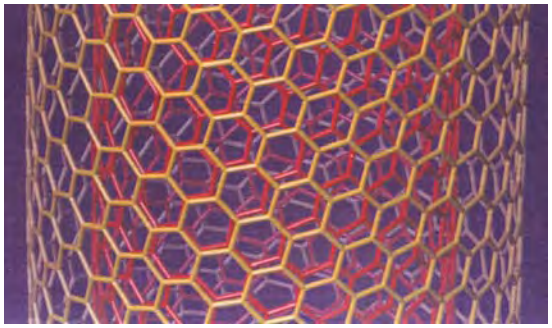




Dimensions

SWNT: 1-2 nm Diameter, Microns Long

MWNT: 2-30 nm Diameter, Microns Long



Structure

Lattice Helicity

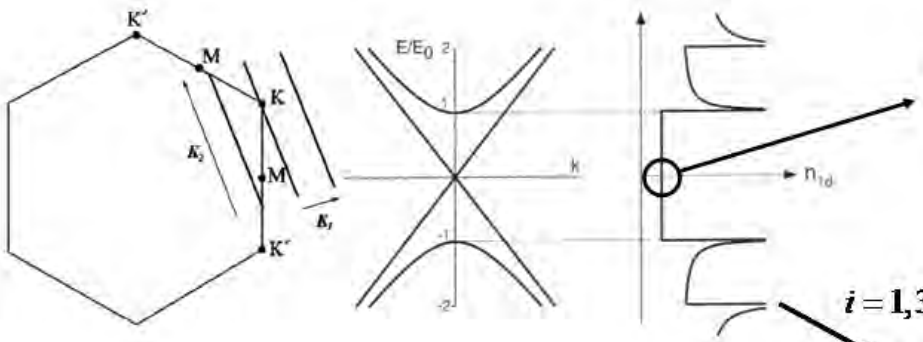
Hollow, Varied Morphology

Capped Ends, Topological Defects

Electronic Structure: Metallic, Semiconductor etc.

Carbon Nanotubes – Electronic Properties

Metallic

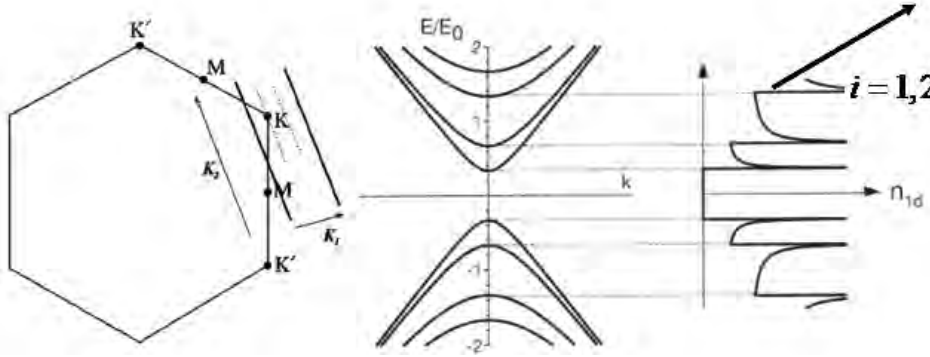


$$G = \frac{4e^2}{h} \approx 6.5k\Omega$$

$$i = 1,3,6$$

$$E_i = i \cdot \frac{2}{3} \cdot \hbar v_F \cdot \frac{1}{d}$$

Semiconducting



$$i = 1,2,4,5,7$$

Mean Free Path – microns

Metallic nanotubes

- Armchair ($n = m$):

- Chiral ($n - m = 3j$): Small band gap (0.1 – 0.01eV)

Applications of Carbon Nanotubes

	Large Volume Applications	Limited Volume Applications (Mostly based on Engineered Nanotube Structures)
Present	- Battery Electrode Additives (MWNT) - Composites (sporting goods; MWNT) - Composites (ESD applications; MWNT)	- Scanning Probe Tips (MWNT) - Specialized Medical Appliances (catheters) (MWNT)
Near Term (less than ten years)	- Battery and Super-capacitor Electrodes - Multifunctional Composites (3D, damping) - Fuel Cell Electrodes (catalyst support) - Transparent Conducting Films - Field Emission Displays / Lighting - CNT based Inks for Printing	- Single Tip Electron Guns - Multi-Tip Array X-ray Sources - Probe Array Test Systems - CNT Brush Contacts - CNT Sensor Devices - Electro-mechanical Memory Device - Thermal Management Systems
Long Term (beyond ten years)	- Power Transmission Cables - Structural Composites (aerospace and automobile etc.) - CNT in Photovoltaic Devices	- Nano-electronics (FET, Interconnects) - Flexible Electronics - CNT based bio-sensors - CNT Fitration/Separation Membranes - Drug-delivery Systems

Endo, Strano and Ajayan on "Applications of Nanotubes"
New Springer book in print on Nanotubes edited by Dresselhaus et al.

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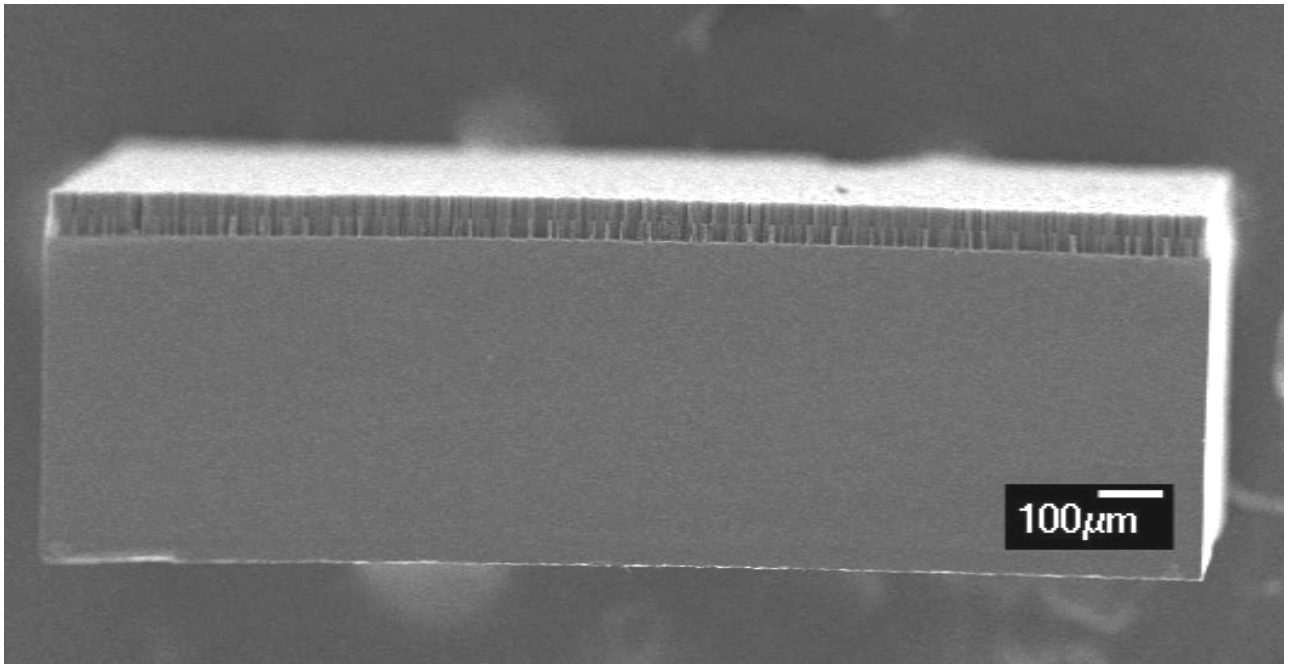
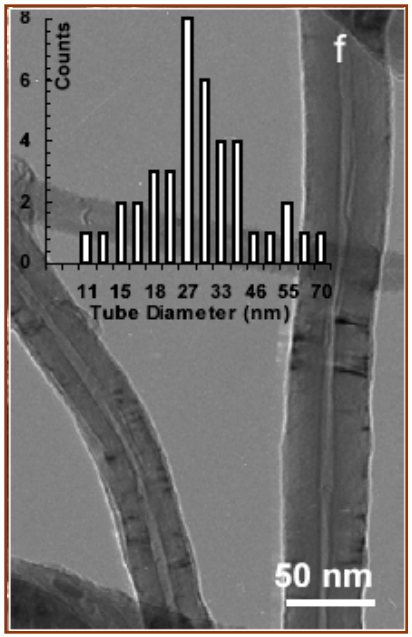
Nanotubes – Dimensional and Structural Variance



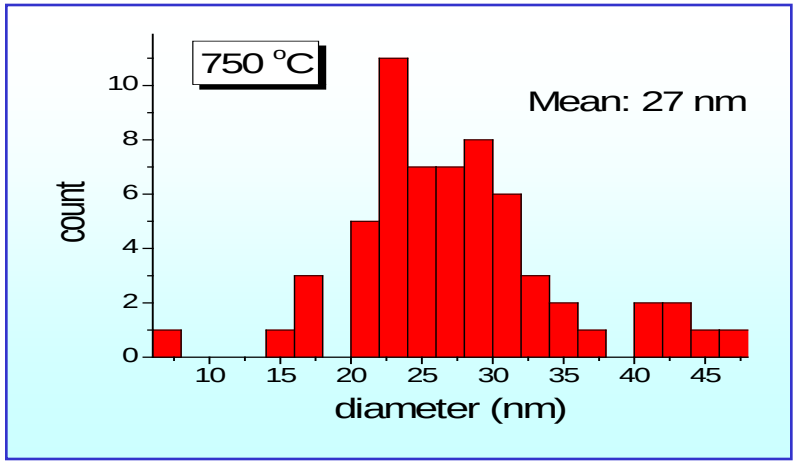


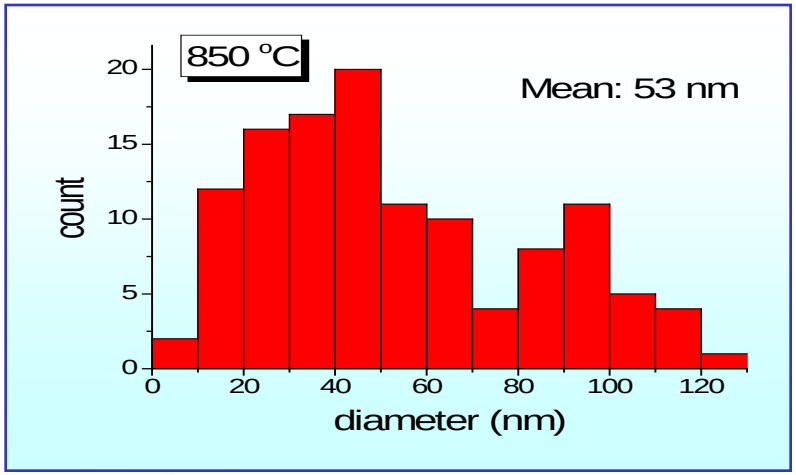
Talapatra, et al., Nature Nanotechnology , 2006

Intrinsic Dimensional and Structural Variance

Diameter distribution - thick MWNT

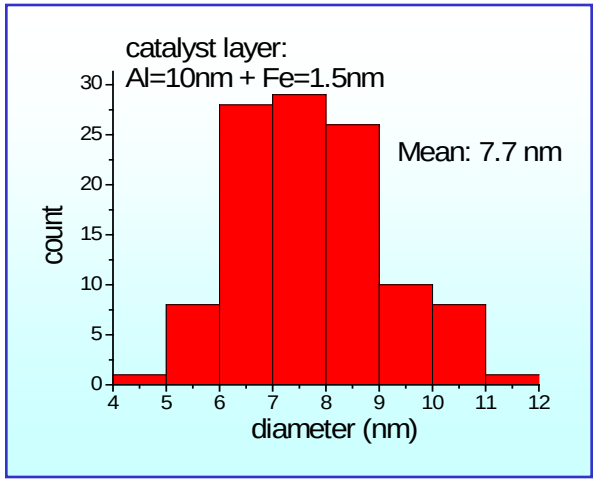
variable: temperature

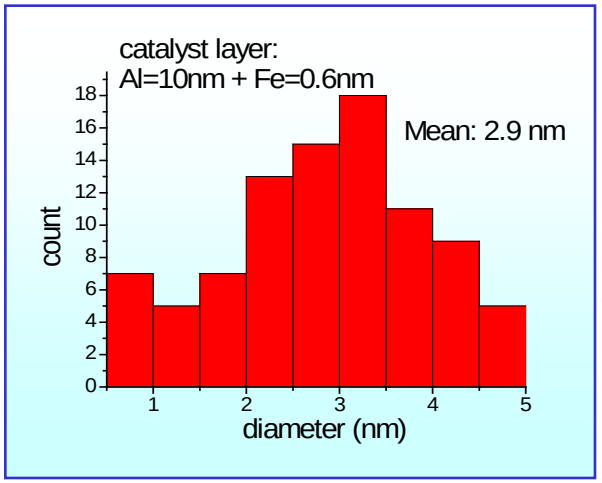




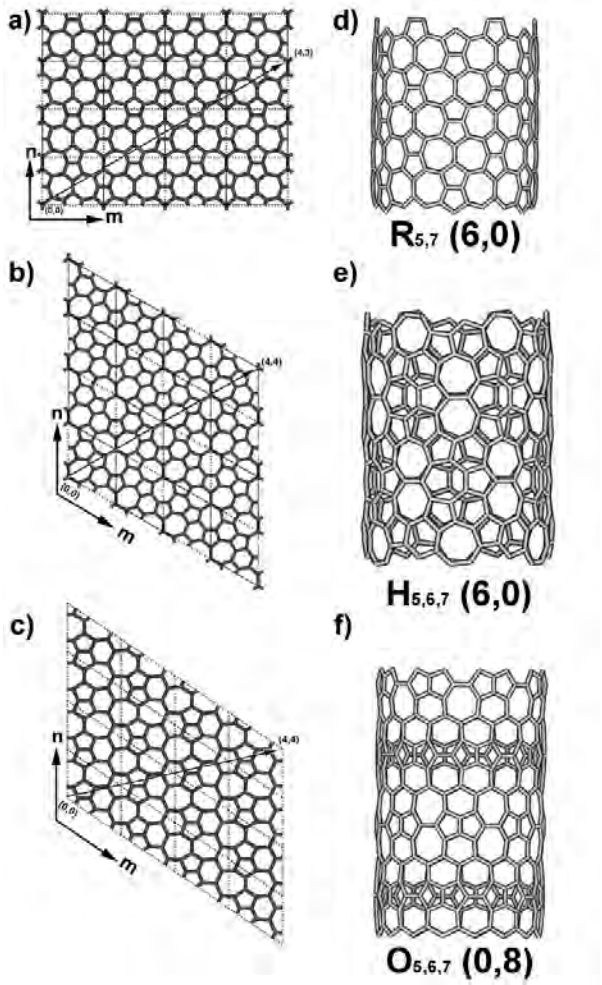
Diameter distribution - thin MWNT

variable: catalyst layer thickness



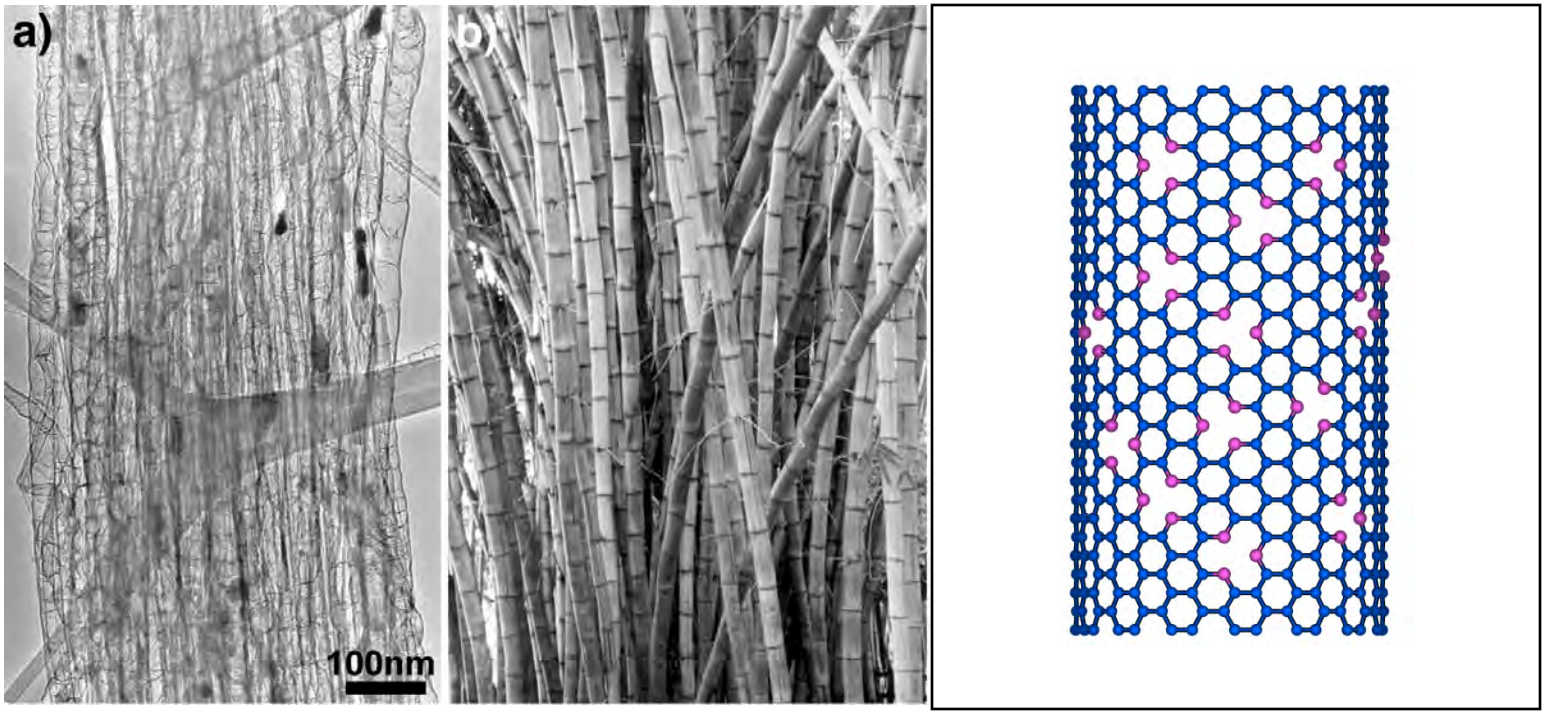


Defects in Nanotubes



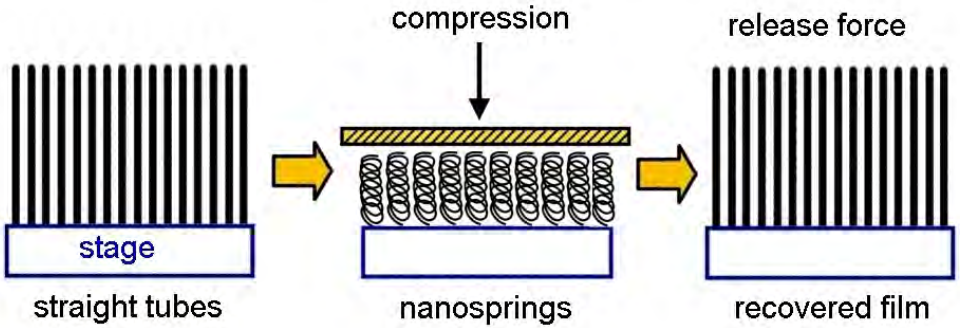
Terrones, Charlier, Ajayan et al., PRL (2000)

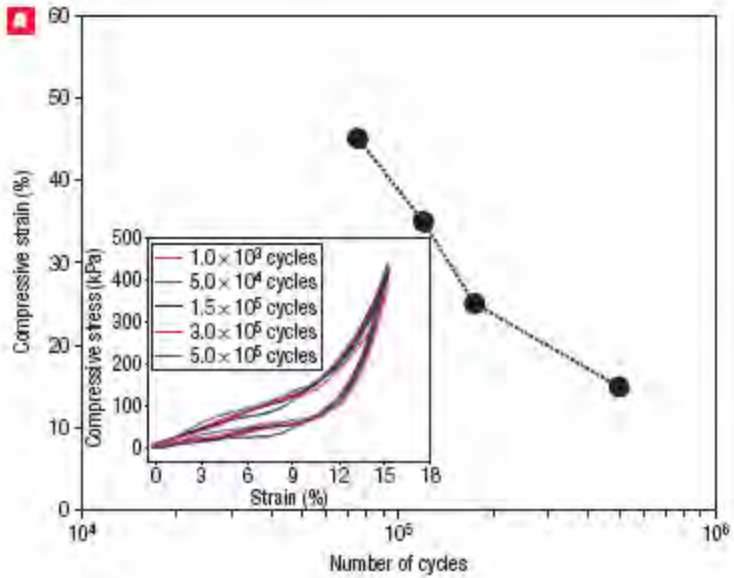
Doping



Nitrogen in CNT

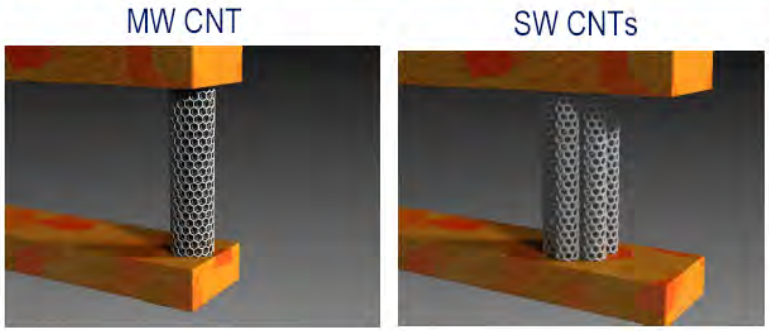
Nanotubes: Mechanical Properties



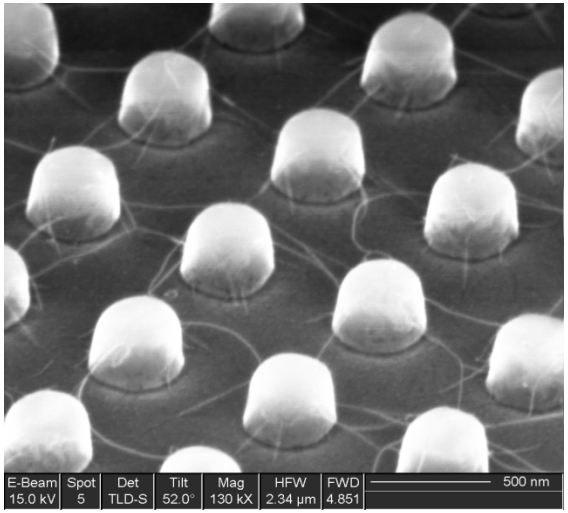


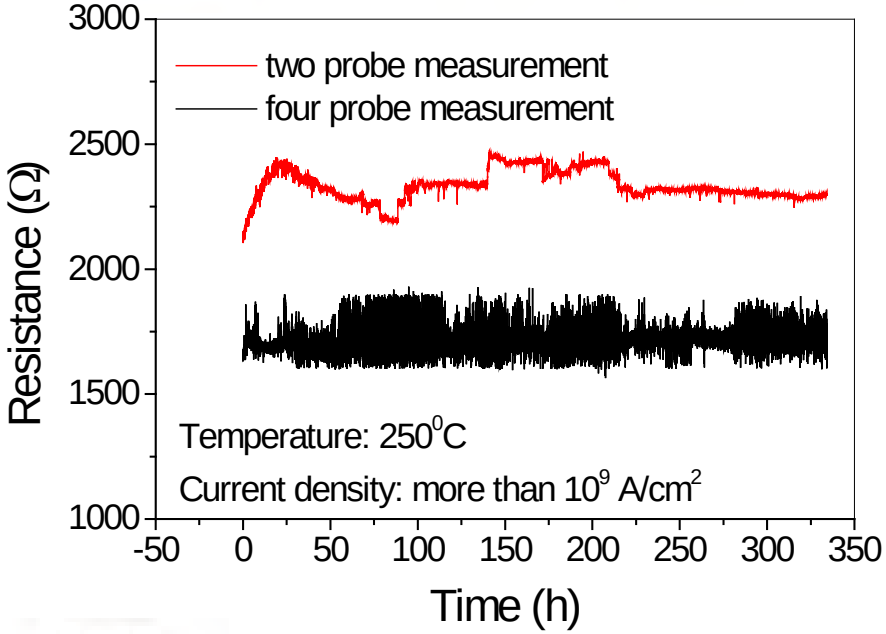
Cao, Ajayan et al., Science (2005)

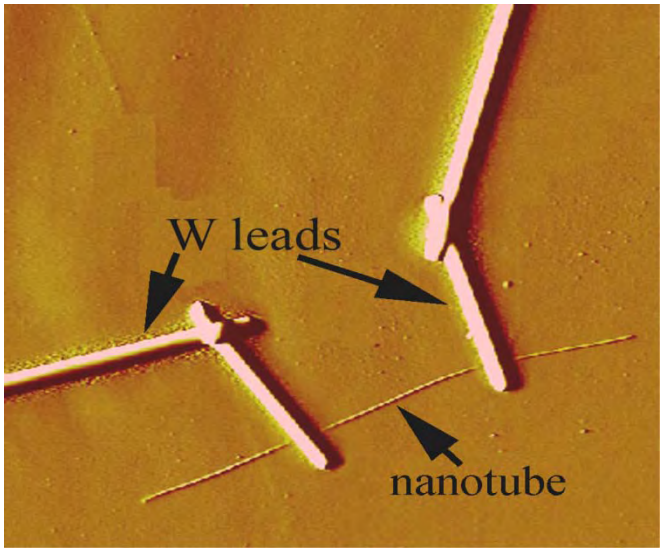
Concept - Carbon Nanotube Via



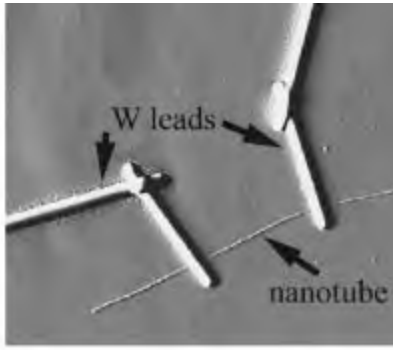
Because of their high structural stability, their thermal conductivity and the ballistic electron transport CNTs will be ideal microelectronic conductors.





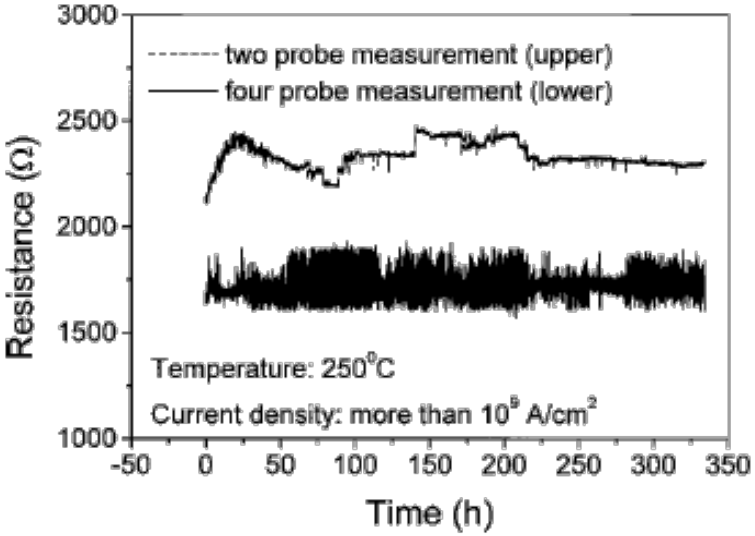


CNT Resistance and Current Carrying Capacity



	Nanotube I	Equivalent Au-wire I	Nanotube II	Equivalent Au-wire II
Diameter	8.6 nm	8.6 nm	15.3 nm	15.3 nm
Length	2.6 μm	2.6 μm	2.5 μm	2.5 μm
Voltage	25 V		17 V	
Resistance	2.4 kΩ	5.6 kΩ	1.7 kΩ	1.0 kΩ
Current density	1.8×10^{10} A/cm^2	–	5.4×10^{9} A/cm^2	–

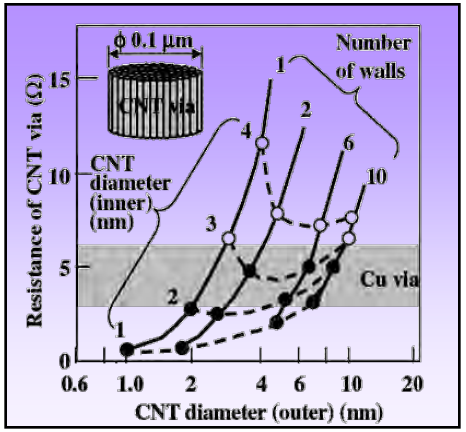
- **No observable change in structure at higher current density**
- **No change in resistance at temperature up to 250 ^{0}C for long time scales**



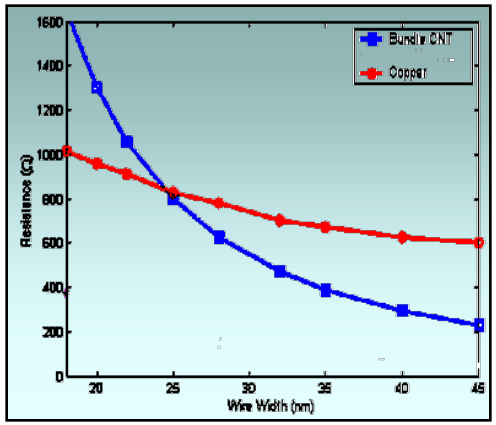
Wei et al. Appl. Phys. Lett. 2001, 79, 1172

Using parallel nanotube architectures for interconnects and VIAs

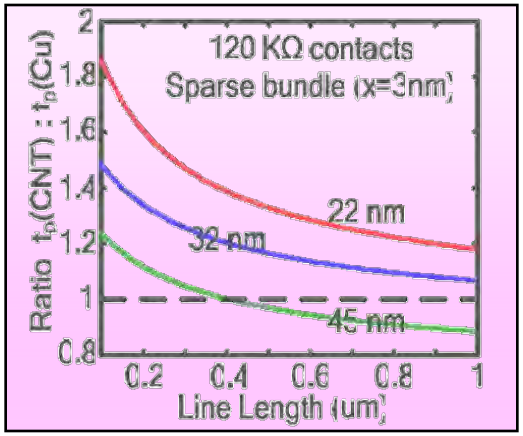
Bundles of nanotubes are expected to perform better than Cu



VIA resistance is less at higher packing density

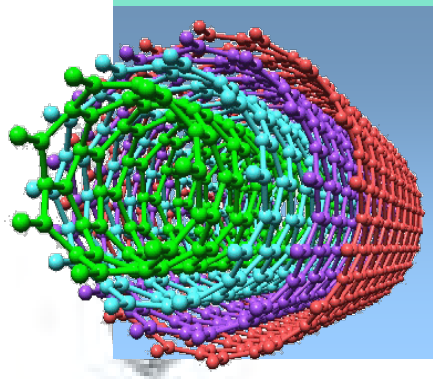


Interconnect resistance is less at larger diameters

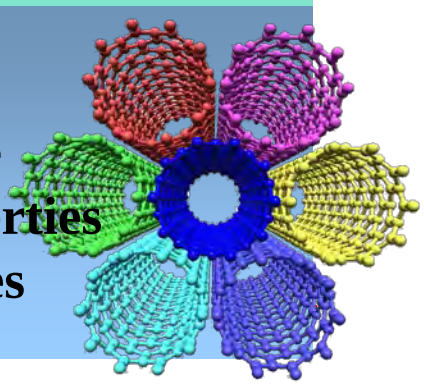


Delay is less for greater lengths

Advantages of using multiple nanotubes in a parallel configuration:



1. Decreases effective interconnect resistance
2. Bundled CNTs have less variance in properties
3. Decrease the effect of quantum impedances



Nihei et al., JJAP 2003; Srivastava & Banerjee, ICCAD 2005

Electrical Properties of MWNTs embedded in silica matrix

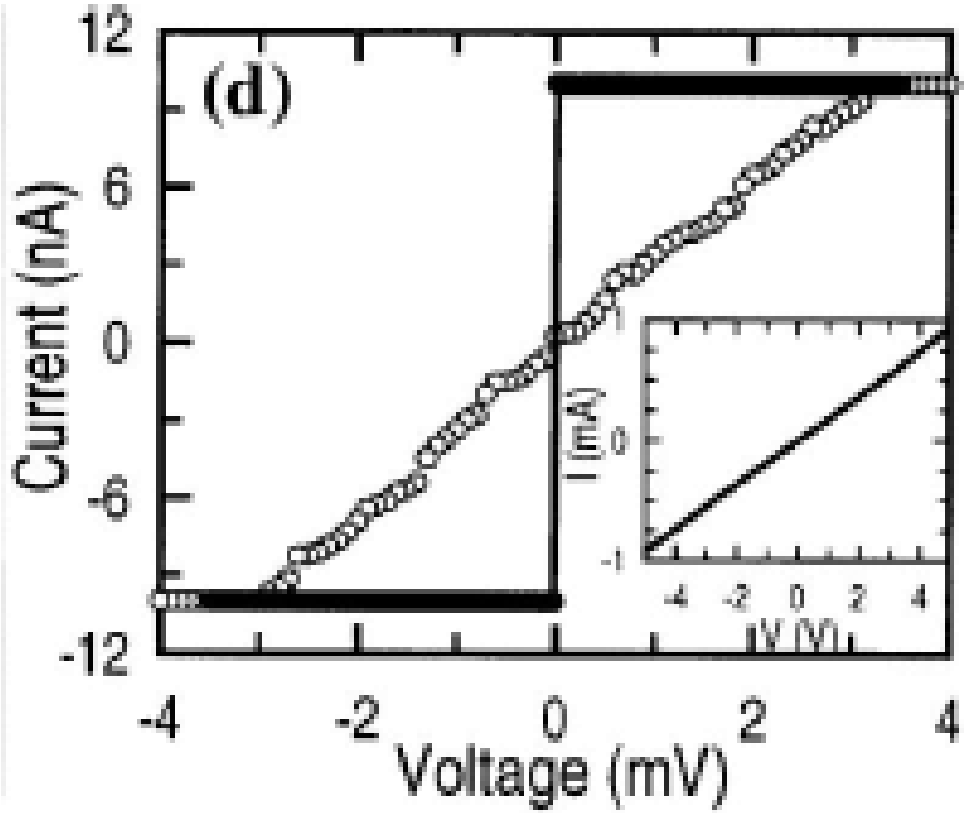
I –V **curve of a single MWNT (open circles) & compact bundle (closed circles)**

The resistance of single MWNT ~ 300 KΩ

The resistance of bundles ~ 2 KΩ

Inset: *I –V* curve of a parallel contacted CNT array measured with a four-probe station

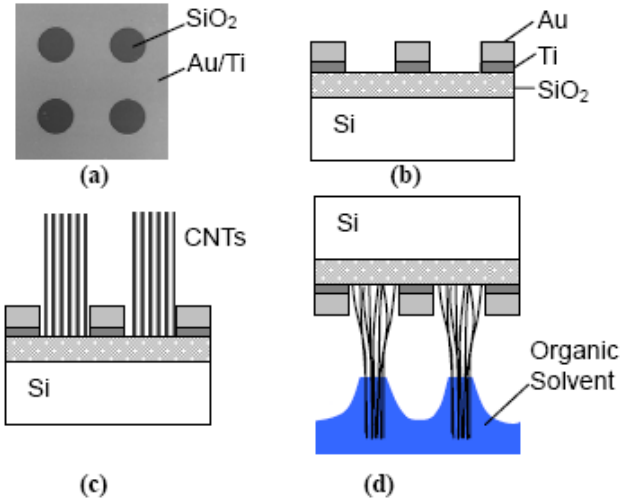
The resistance of 60 MWNT~ 5.2 KΩ

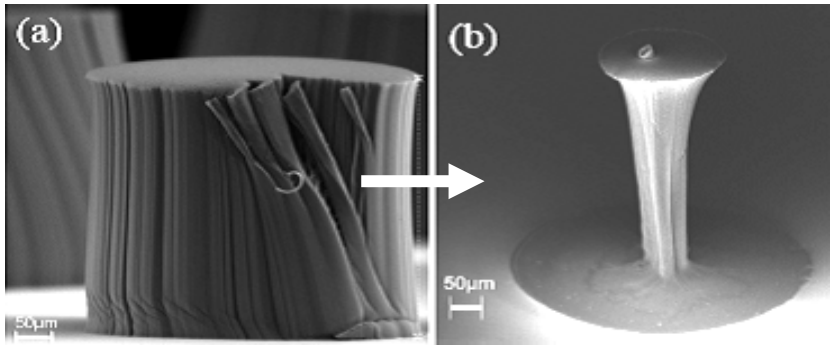


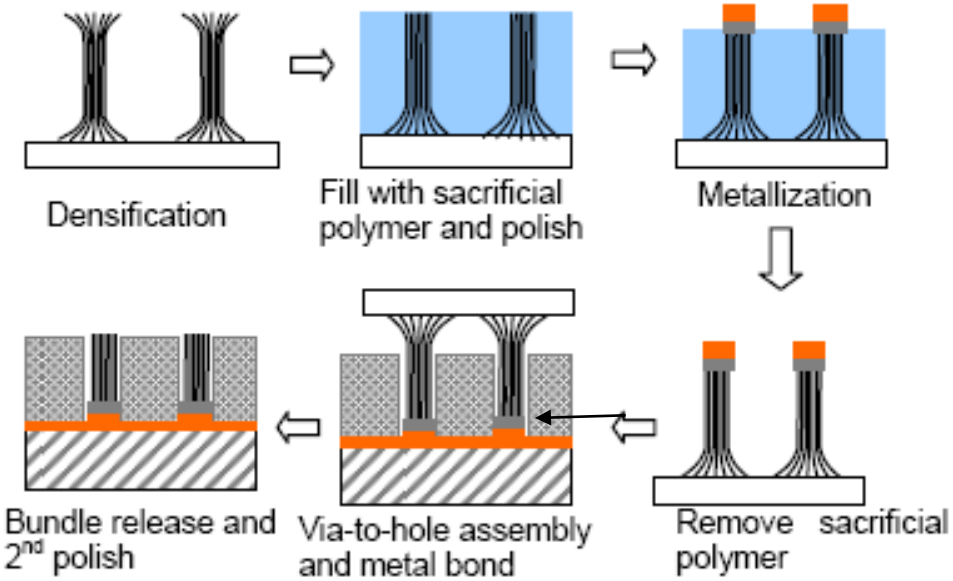
Li et al. Appl. Phys. Lett. 2003, 82, 2491

Resistance: Experimental (300 KΩ) vs. Theoritical (12.9 KΩ)

CNT Vias – the density issue

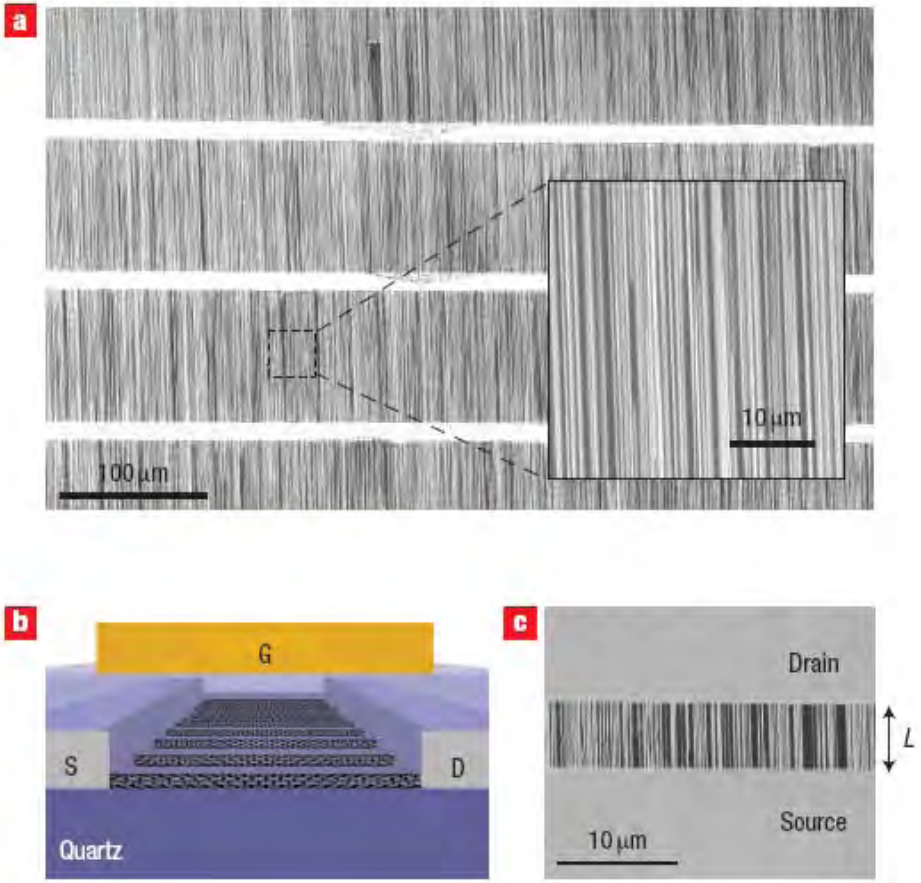






Z. Liu et al., IEEE-IITC Proceeding (2007)

Assembly – Achieving High Density



JOHN A. ROGERS and coworkers, NATURE NANOTECHNOLOGY , 2007

Design and Performance Modeling for Single-Walled Carbon Nanotubes as Local, semiglobal, and Global Interconnects in Gigascale Integrated Systems

Using distributed circuit models for single-walled carbon nanotubes (SWCNs) and SWCN bundles that are valid for all voltages and lengths, it has been shown that customizing SWCN interconnects at the local, semiglobal, and global levels, several major challenges facing gigascale integrated systems can potentially be addressed.

- **For local interconnects, monolayer or multilayer SWCN interconnects can offer up to 50% reduction in capacitance and power dissipation with up to 20% improvement in latency if they are short enough (< *20 μm*).**
- **For semiglobal interconnects, either latency or power dissipation can be substantially improved if bundles of SWCNs are used.**
- **The improvements increase as the cross-sectional dimensions scale down. For global interconnects, bandwidth density can be improved by 40% if there is at least one metallic SWCN per 3-nm^2 cross-sectional area.**

Azad Naeemi, *and James D. Meindl,* IEEE TRANSACTIONS ON ELECTRON DEVICES, VOL. 54, NO. 1, JANUARY 2007

RICE

Compact Physical Models for CNT Interconnects

Compact physical models for conductivity of multiwall carbon-nanotube (MWCN) interconnects.

- **For MWCNs shorter than the critical length (typically around 7 *μm), the conductivity decreases as diameter increases***
- **For MWCNs longer than the critical length, increasing the diameter results in higher conductivities.**
- **For long lengths (hundreds of micrometers), MWCNs can potentially have conductivities several times larger than that of copper or even single-wall carbon nanotube (SWCN) bundles.**
- **For short lengths (< *10 μm)*, however, SWCN bundles offer more than two times higher conductivities compared to MWCNs.**

Azad Naeemi, *and James D. Meindl,* IEEE ELECTRON DEVICE LETTERS, VOL. 27, NO. 5, MAY 2006

RICE

Microwave Impedance Spectroscopy of Dense Carbon Nanotube Bundles

Alexander Tselev, Michael Woodson, Cheng Qian, and Jie Liu*

NANO LETTERS 2008 Vol. 8, No. 1 152-156

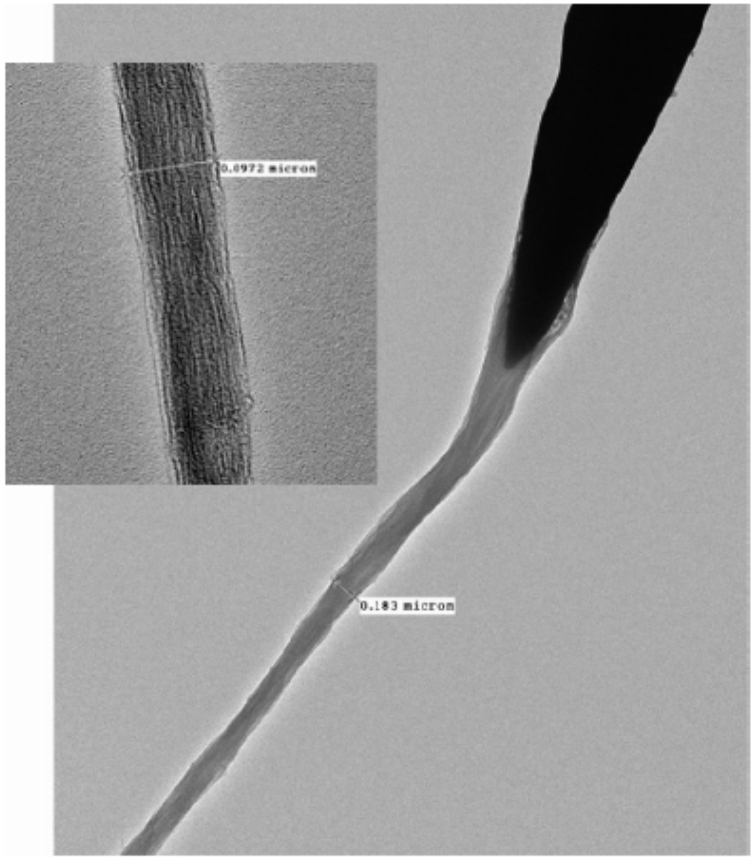


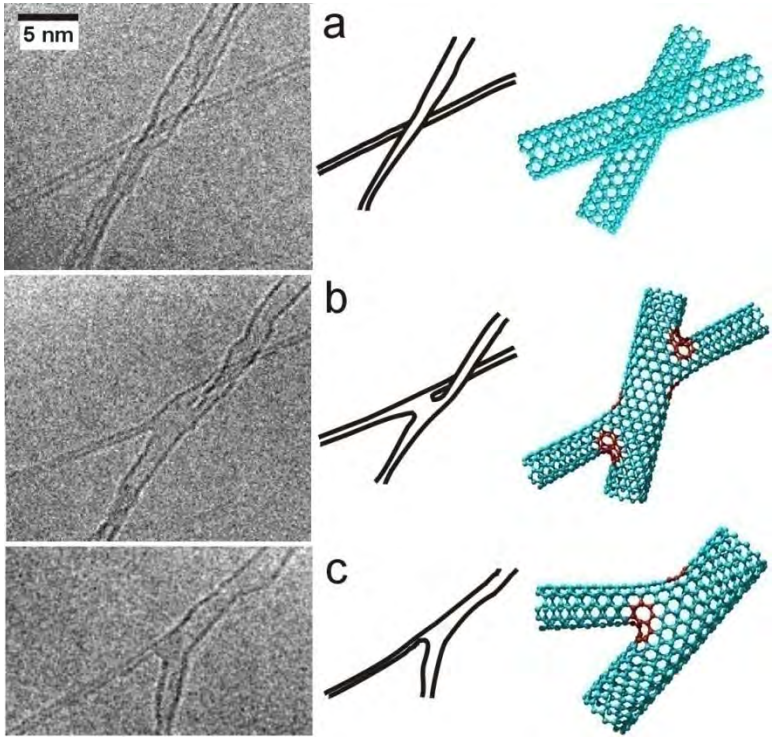
Figure 1. A dense CNT bundle attached to an indium tip. The bundle diameter at the white mark is 180 nm. Inset: A part of the bundle away from the root at higher magnification. The bundle diameter in the inset is 100 nm.

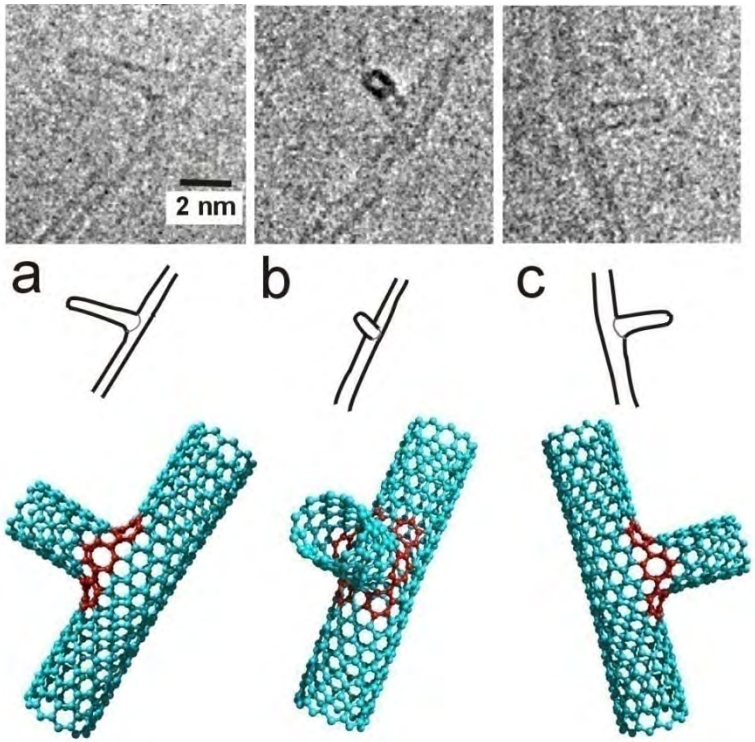
Impedance spectroscopy of dense carbon nanotube (CNT) bundles in the broad frequency range from 10 MHz to 67 GHz.

The frequency response of the bundles can be fit to a model with frequency-independent elements in the entire frequency range up to 67 GHz strongly suggesting that CNT properties do not depend on the frequency throughout the whole frequency range.

For good quality nanotube bundles, the inductance has been found to fall within the range from approximately 3.5 to 40 nH/*μm*.

Materials Challenges: Junctions

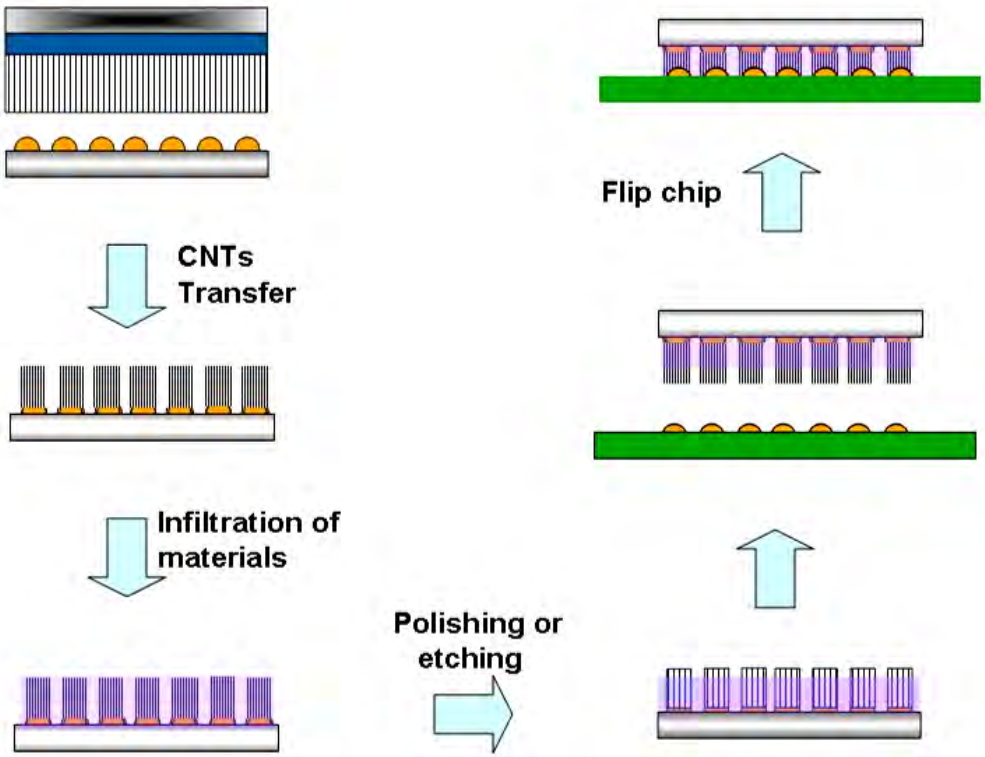


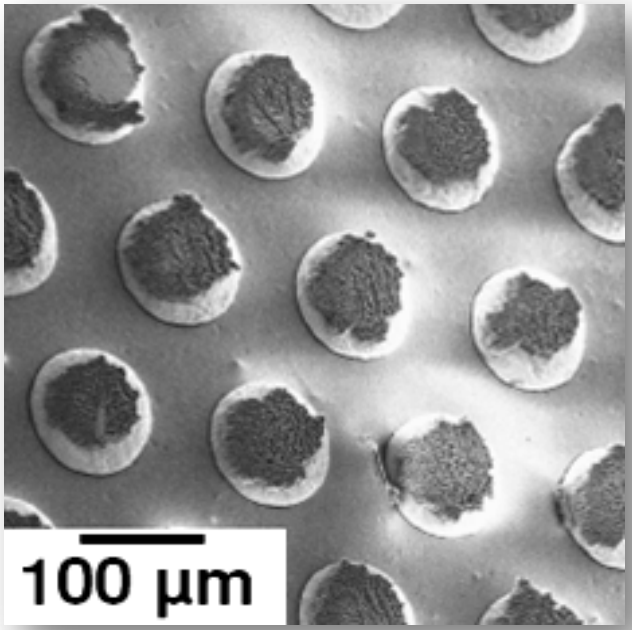


Terrones, Banhart, Ajayan, PRL, 2002, 2004

The Interface Issue

low temperature process for VIA end-metallization and transfer from insulating growth platforms to metallic pads





CNT arrays transferred onto low-T solder bumps without losing alignment

Kumar, Ajayan, Baskaran et al., App. Phys. Letters, 89, 163120 (2006)

- Collaboration with Intel -

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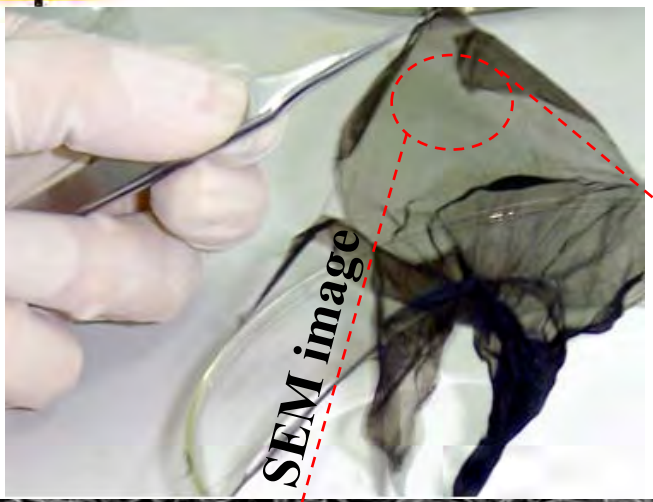
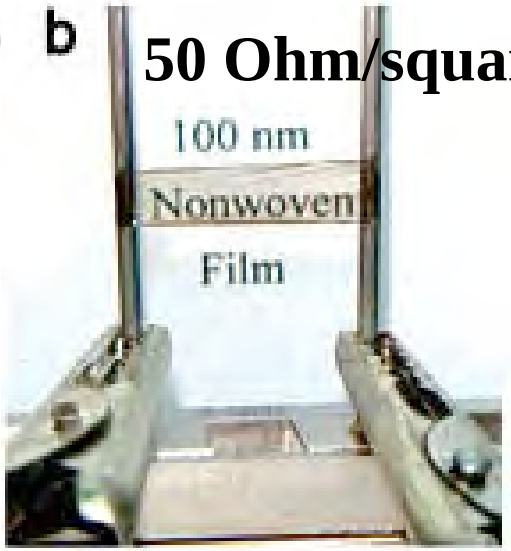
SWNTs Films and Fibers

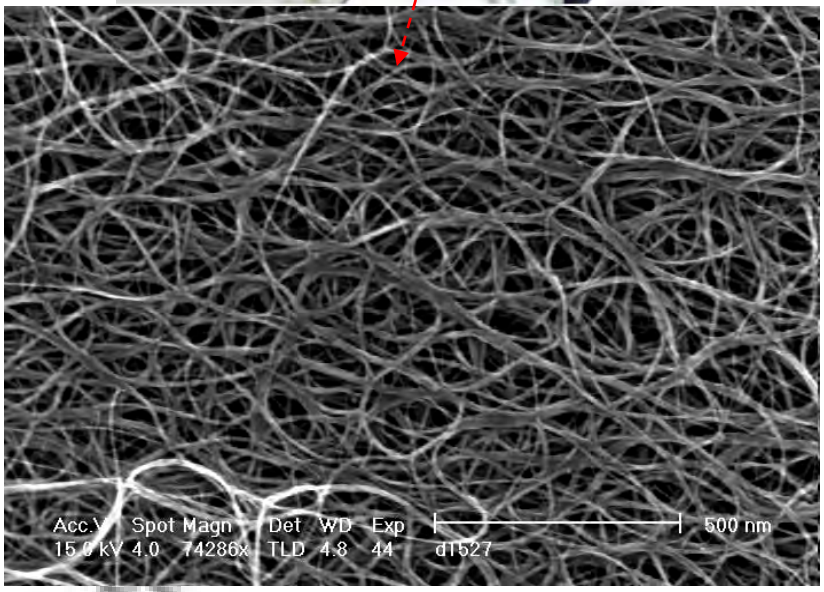


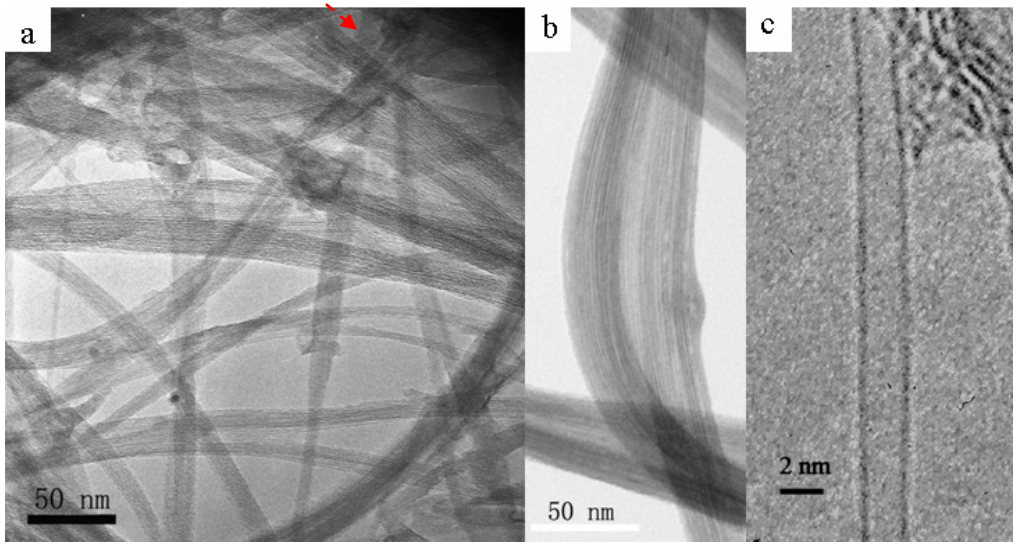
SEM image

TEM image

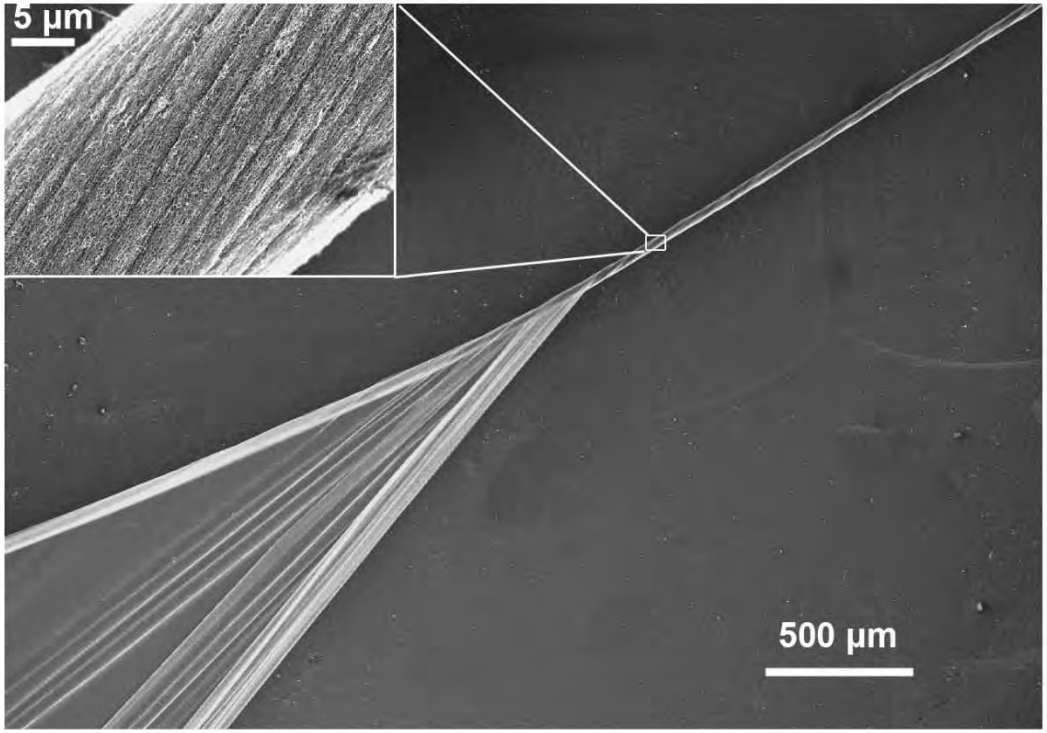


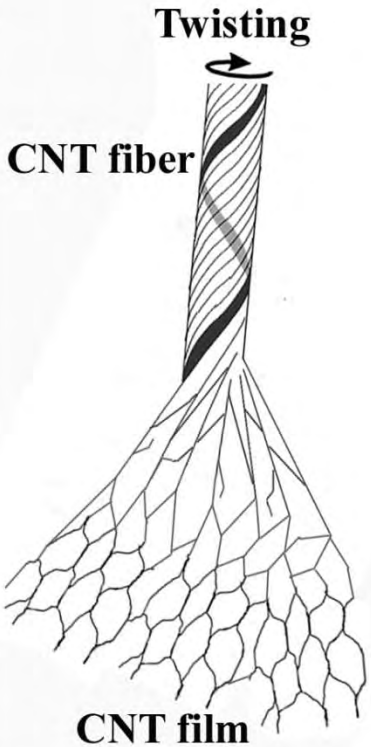
50 Ohm/square

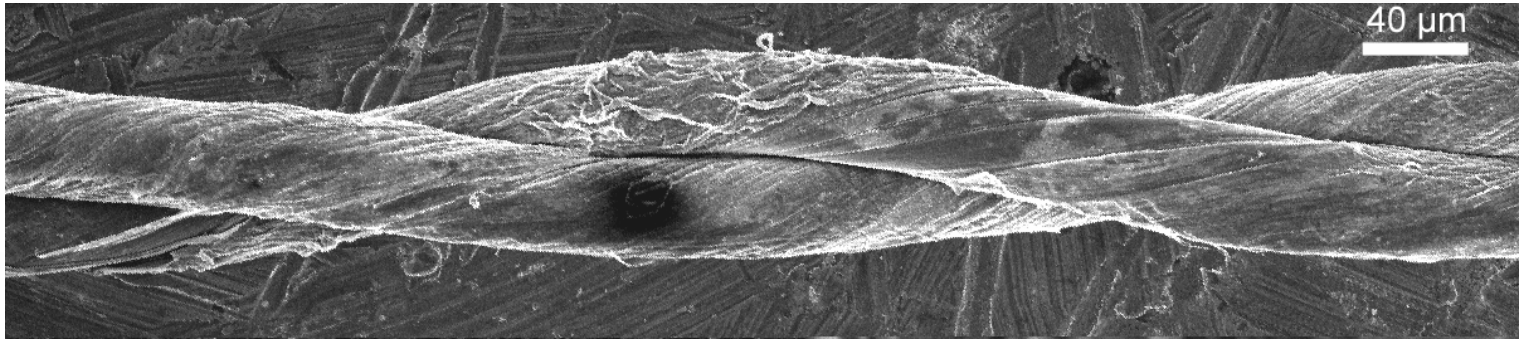




Ma, Song, et al, ***Nano Lett. 2007***,*7*,*2307*







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Conduction in Nanotubes: Materials Challenges

- Individual nanotubes (metallic) are highly conducting
- Formation of bundles are advantageous
- Density issues are important
- Large bundles (cables) fall short of promises
- New approaches to increase conductivity needed
- Multi-functionality of nanotubes could be selling point

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Financial Support

Interconnect Focus Center (DARPA, MARCO)
Hartley Foundation
NSF NIRT, NSF (DMR)
ARL, AFRL, RPSEA
ONR, DOE, NIH

Acknowledgments

Post-docs: **L. Ci, A. Kumar, L. Song**
Students: **F. S. Ou, A. Vijayaraghavan, S. Pal**
Collaborators: **R. Vajtai, S. Talapatra, R. Baskaran, S. Kilpatrick, N. Koratkar, S. Kar, S. Sahoo, M. Terrones**

RICE

nanoUmbilical
Workshop

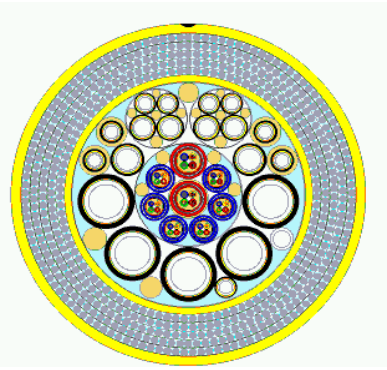
Need for Lightweight Umbilicals

Dave Madden – Senior Technical Manager DUCO Inc.

AGENDA

- Umbilicals
- Offshore hosts & arrangements
- Dynamic umbilicals
- Power cable umbilicals
- RPSEA Initiative
- Cable & umbilical comparisons
- Installation
- Possible applications
- Conclusions

What is an Umbilical ?

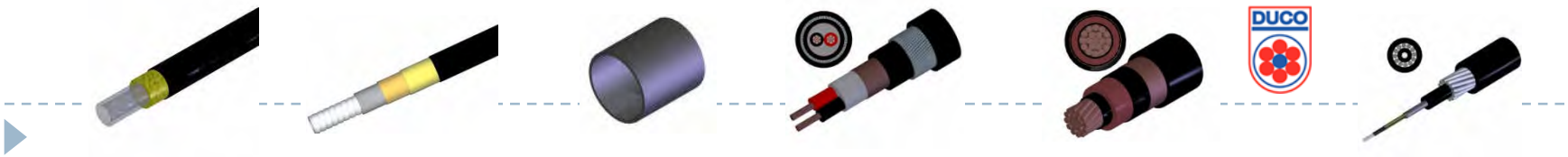


- **Umbilical**
  - **A number of functional components contained within a flexible package.**

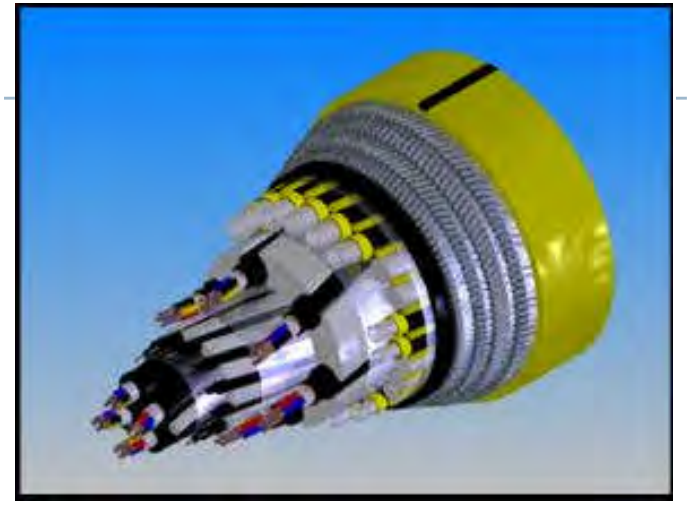
    Typically the flexible package comprises of a thermoplastic extruded layer, surrounding a bundle of functional components which are assembled together in a compact structure. The flexible package may also be armored or contain tensile/weight members.

    <u>Not</u> a line to transport recovered hydrocarbons !

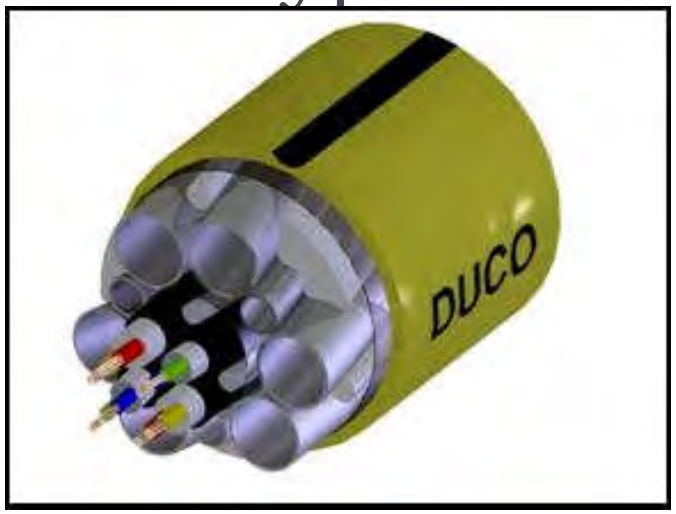
- **Functional Components ?**
  - Components included within the umbilical which are required to fulfill the system operational needs, such as :-
    - **Hoses / Tubes**
    - **Electrical and Optical Fiber Cables**



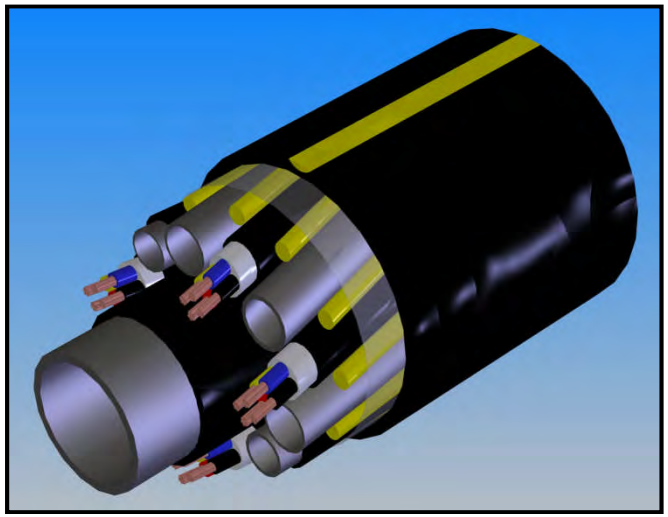
DUCO Umbilical Types



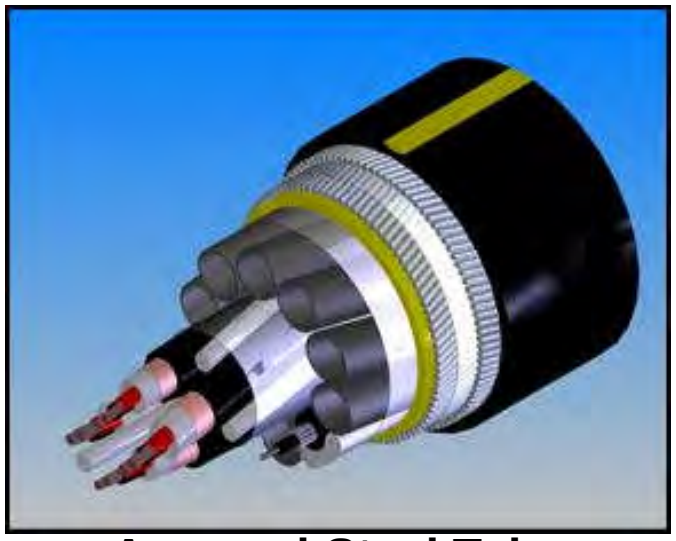
Thermoplastic Hose



Steel Tube

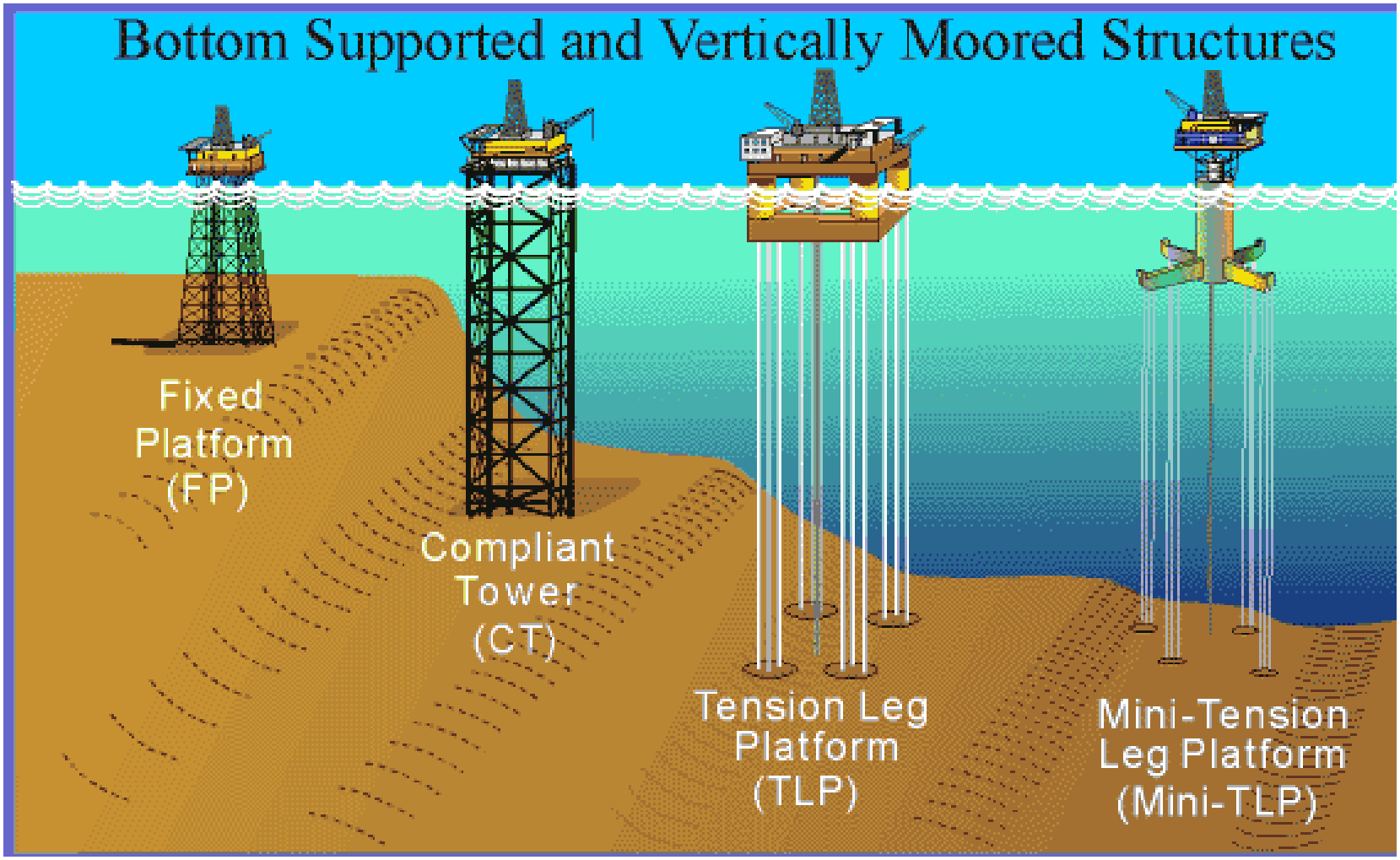


Large Central Tube

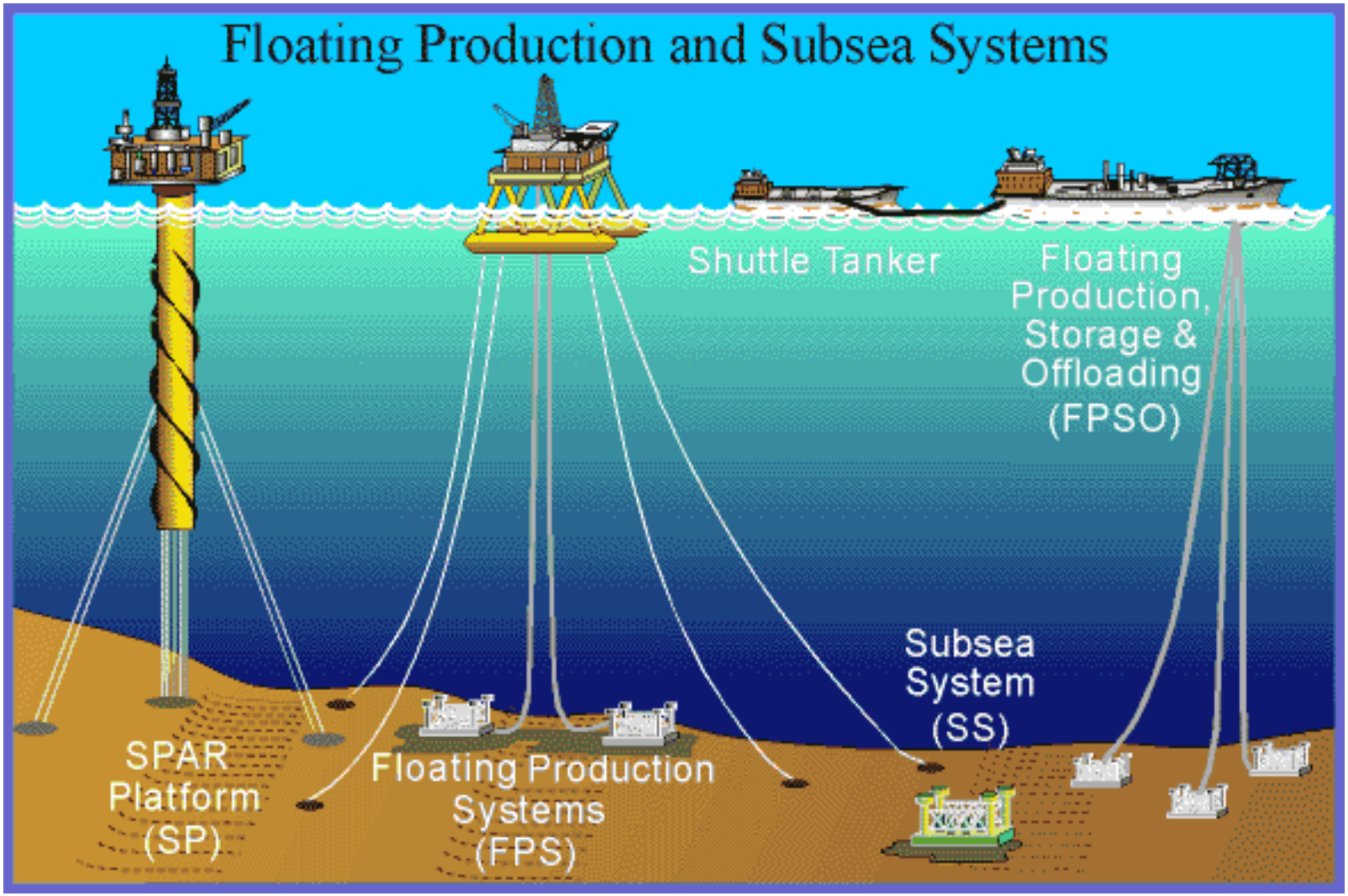


Armored Steel Tube

Offshore Host's – Rigs, Platforms & Vessels



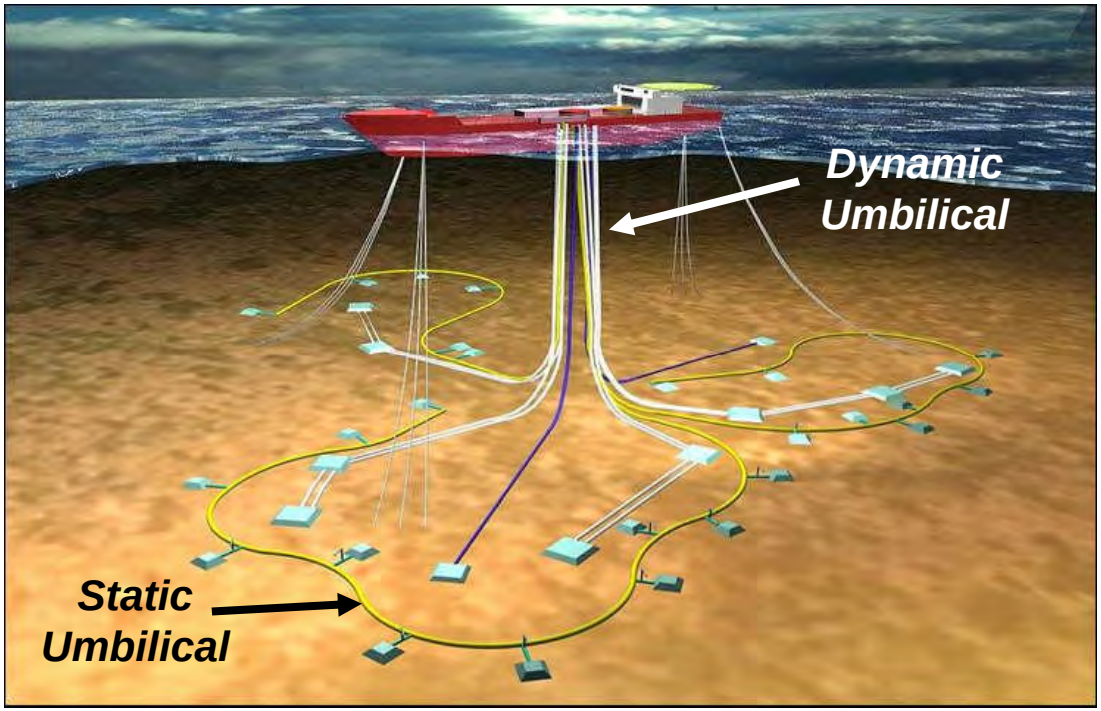
Offshore Host's – Rigs, Platforms & Vessels



System Arrangement

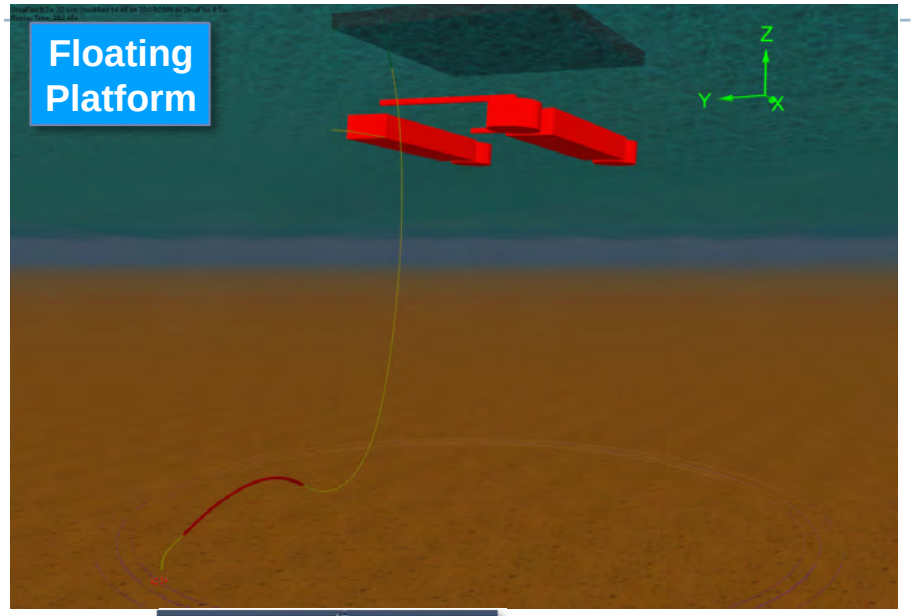
- Supply and control link to sub-sea equipment

- Design Criteria
  - Static
    - Mechanical
    - Thermal
    - Electrical
    - Hydraulic
    - Environmental
      - Seabed stability
  - Dynamic
    (in addition to static)
    - Environmental
    - Vessel motion
      - Dynamic motion & fatigue

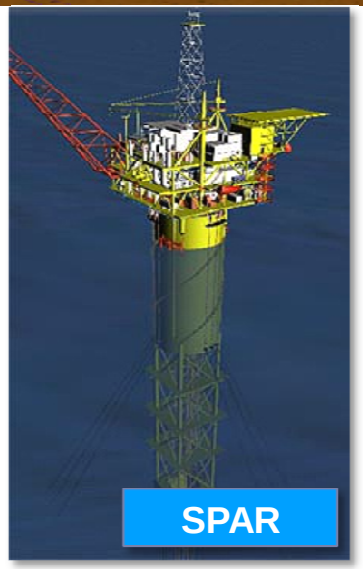


Dynamic Umbilical Considerations

- Shallow Water
  - Installation
    - Low topside tension
    - High dynamic wave motion
  - Design considerations for static and dynamic applications are most different.

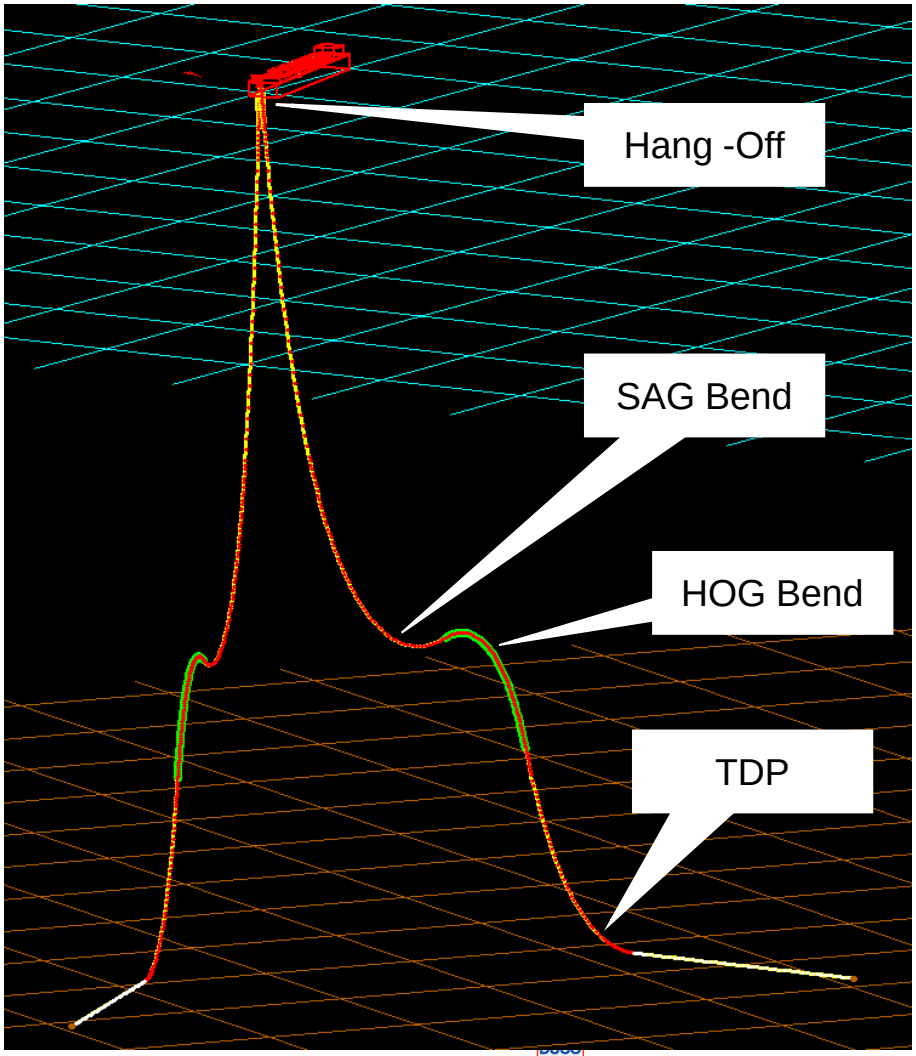


- Deep Water
  - Installation
    - High topside tension
    - Low dynamic wave motion
  - Differences between static and dynamic solutions may be more subtle

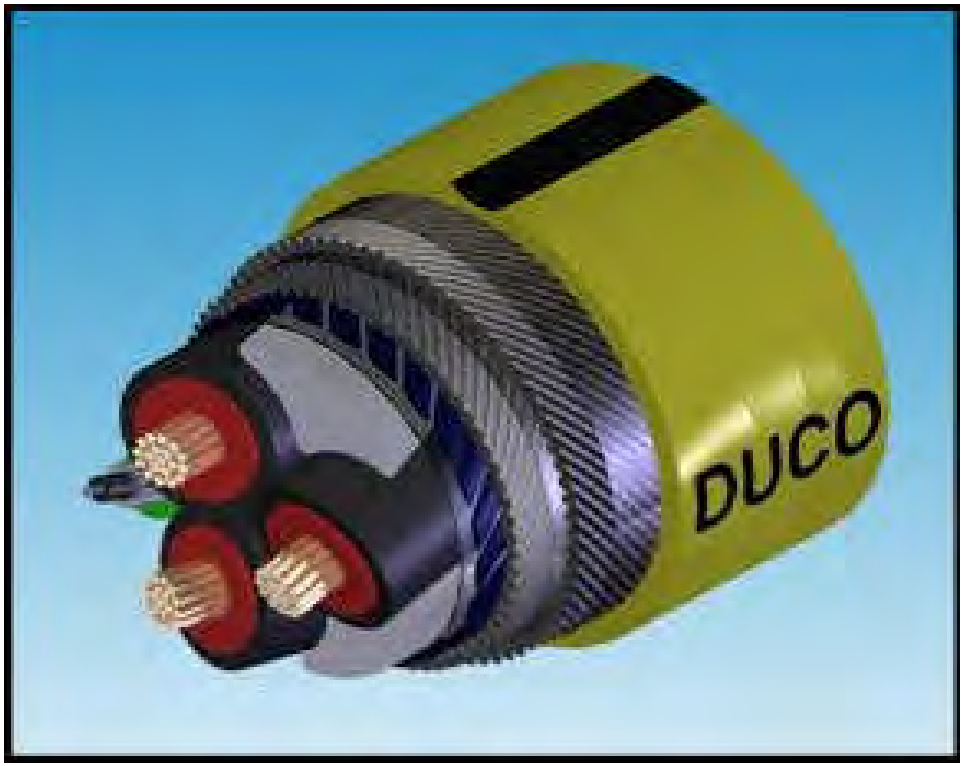


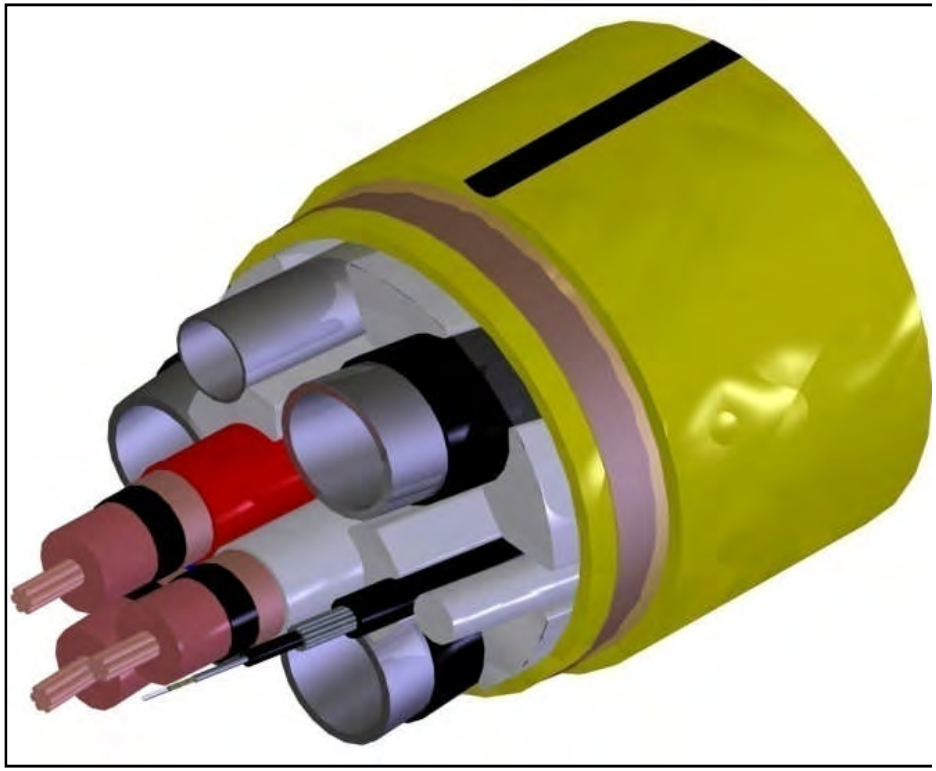
Dynamic Umbilical Configuration

- Load variations assessed along the riser length; tension variations (self weight and dynamic effects) and curvature variations.
- Design assessed against various environmental return periods, e.g. FPSO ballast conditions, FPSO extreme motions and mooring line failure.
- Tension and curvatures assessed at Hang-off, Sag Bend, Hog Bend, and TDP



Power Cable Umbilicals





Power Systems / Coms

Utility

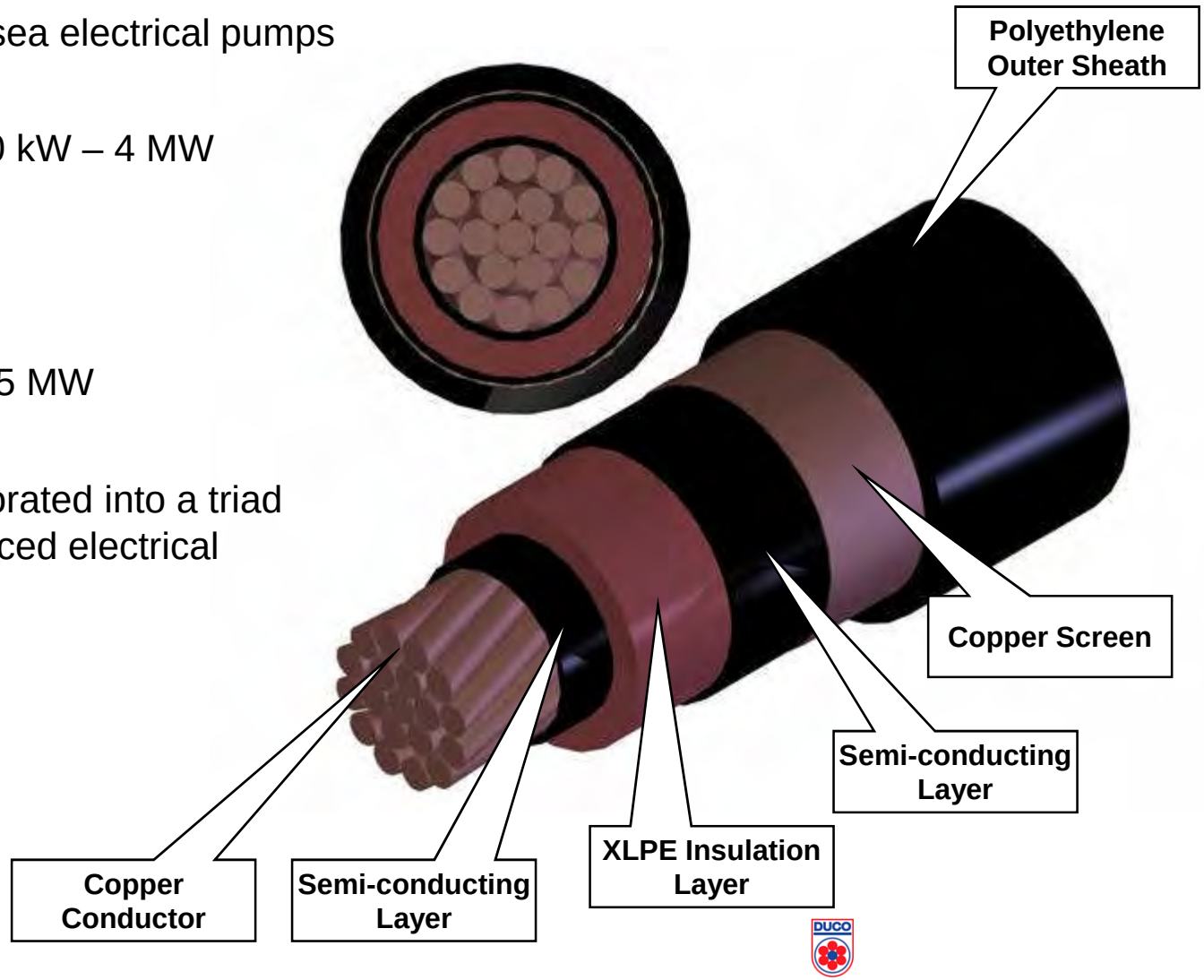
Increasing need to deliver electrical power subsea

MV Electrical Power Cable

- Artificial Lift using subsea electrical pumps
  3 Phase power,
  Typically 6.6kV, 500 kW – 4 MW

- Platform to Platform
  3 Phase power,
  Typically >11kV, > 5 MW

- The cables are incorporated into a triad configuration for balanced electrical characteristics



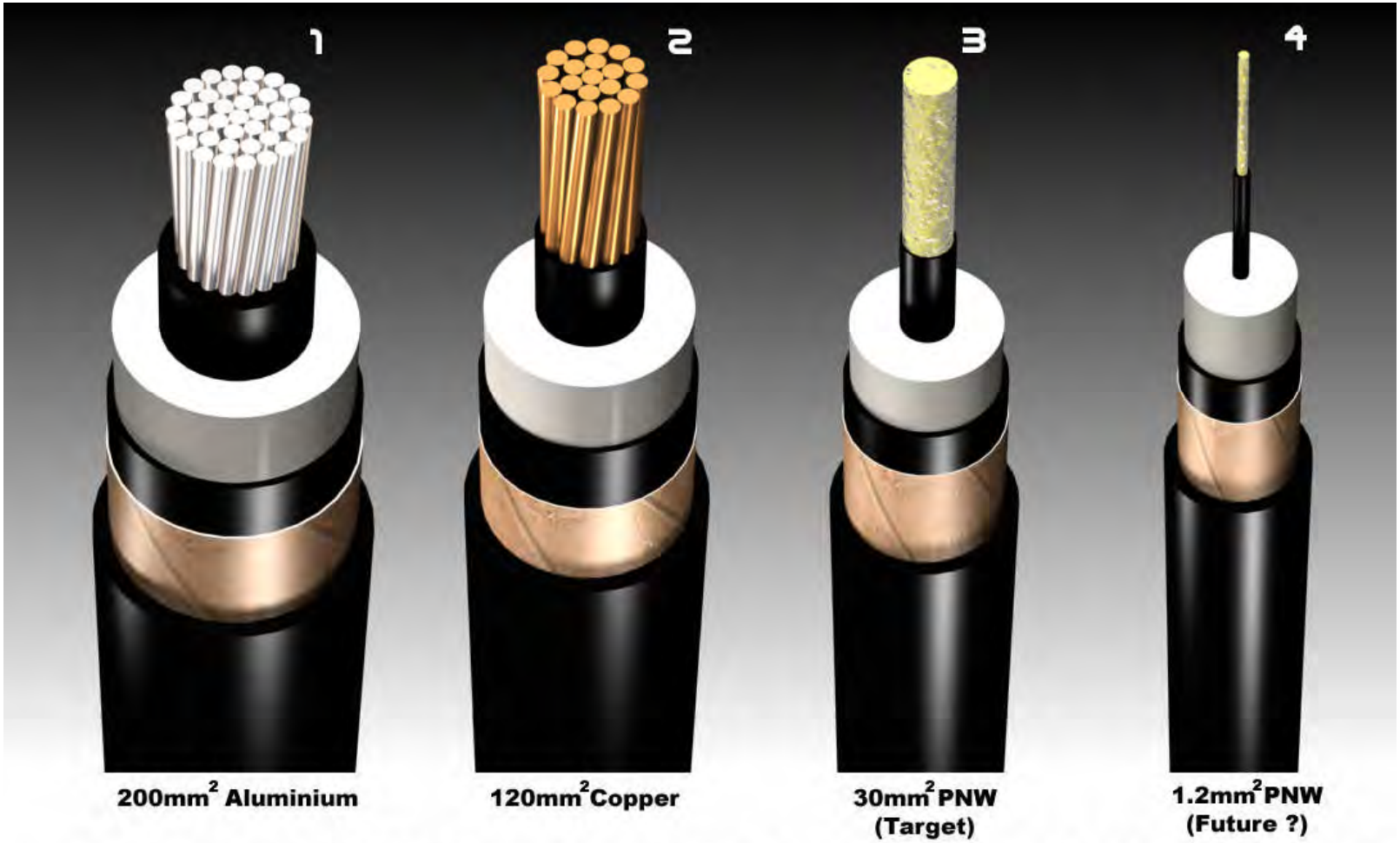
RPSEA Initiative

- The RPSEA goal is to provide an ultra-high conductivity wire that has the ability to carry at least 500 Amps at room temperature, and be half the diameter of a pure copper conductor carrying the same current at the same voltage.

- 120mm^2 copper conductor was selected as the reference for evaluation, based on relevant industry standards for the application. An aluminium cable of equivalent conductivity was also included for information.

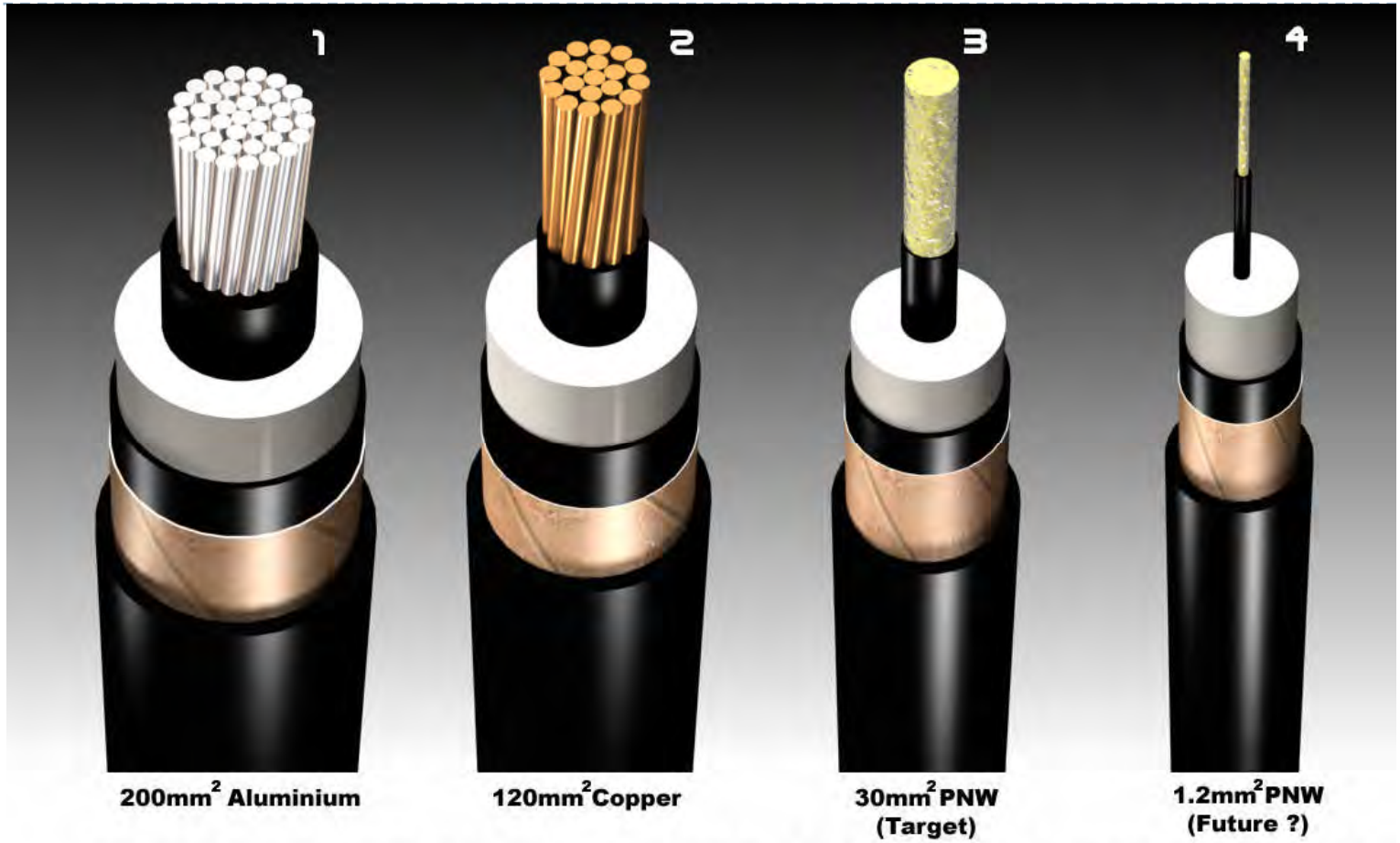
- No consideration was given to voltage, so a typical system insulation rating of 12/20 kV was assumed for the purposes of any further analysis, with copper screen tapes applied.

Comparison of MV Power Cables



SCREENED POWER CABLES WITH 12/20kV XLPE INSULATION

Comparison of MV Power Cables



Diameter (mm)	38	33	25	19
Wt in Air (kg/m)	1.45	1.82	0.54	0.33
Wt in Water (kg/m)	0.29	0.96	0.03	0.02

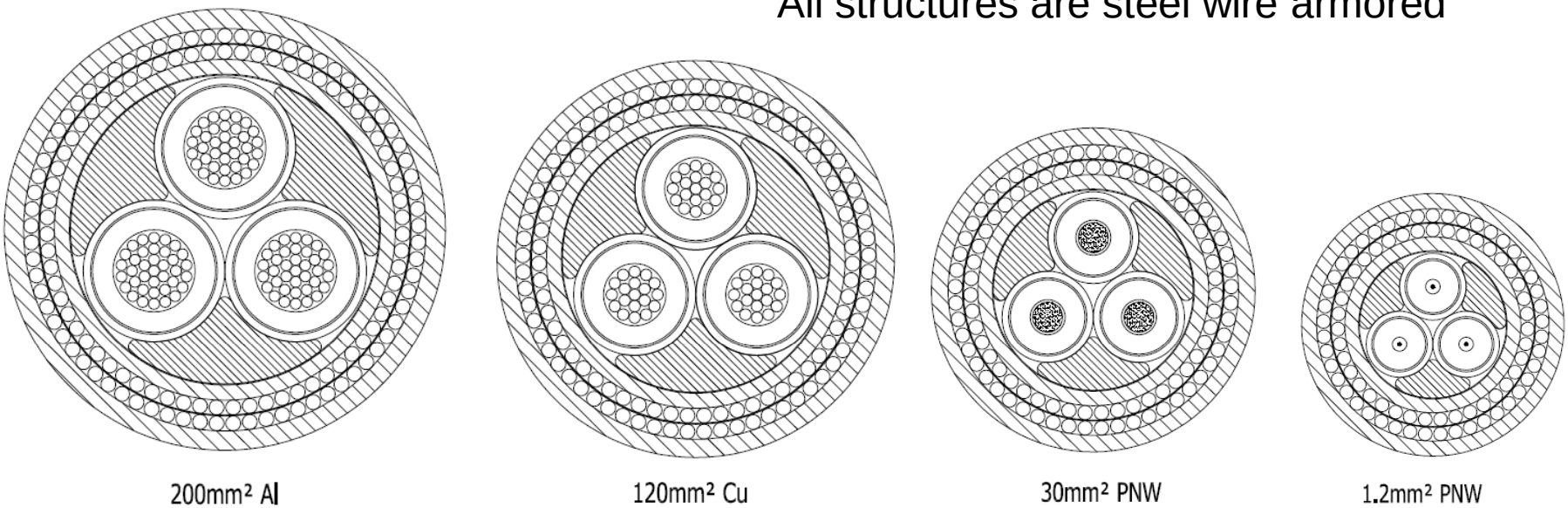
Power Cable Umbilical Design

- By assembling the various articles used in the comparison, into a ‘classical’ single power cable umbilical it is possible to compare the differences due to changes in conductor material alone.

- In the classical design, steel wire (double layer for torque balance) armoring and standard sheathing thicknesses’ have been assumed.

Comparison of Power Umbilicals

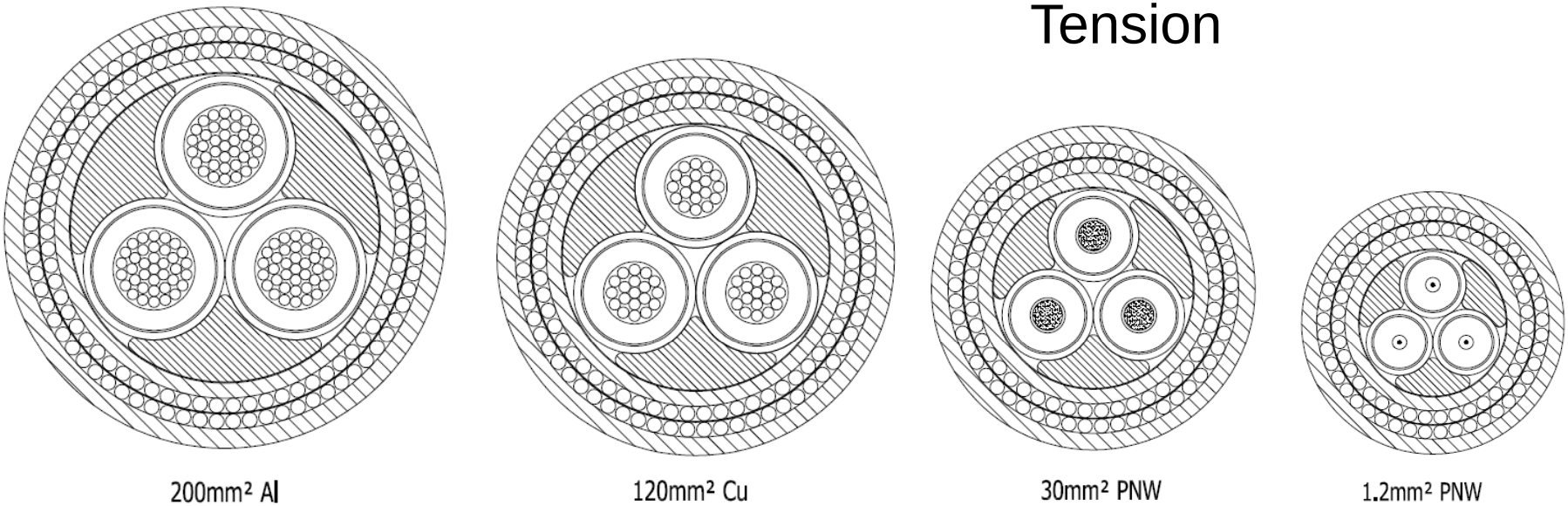
All structures are steel wire armored



Dia (mm)	118	106	90	77
Wt (kg/m)	23.3	21.9	14.5	11.6
Wt (kg/m) in water	12.9	13.6	8.7	7.3

Comparison of Power Umbilicals

Tension



Top tensions during Installation at various water depths

Depth	Top tension in Tonnes			
3,000’	17	18	12	10
6,000’	34	36	23	20
10,000’	57	60	38	32

Strain Limitation

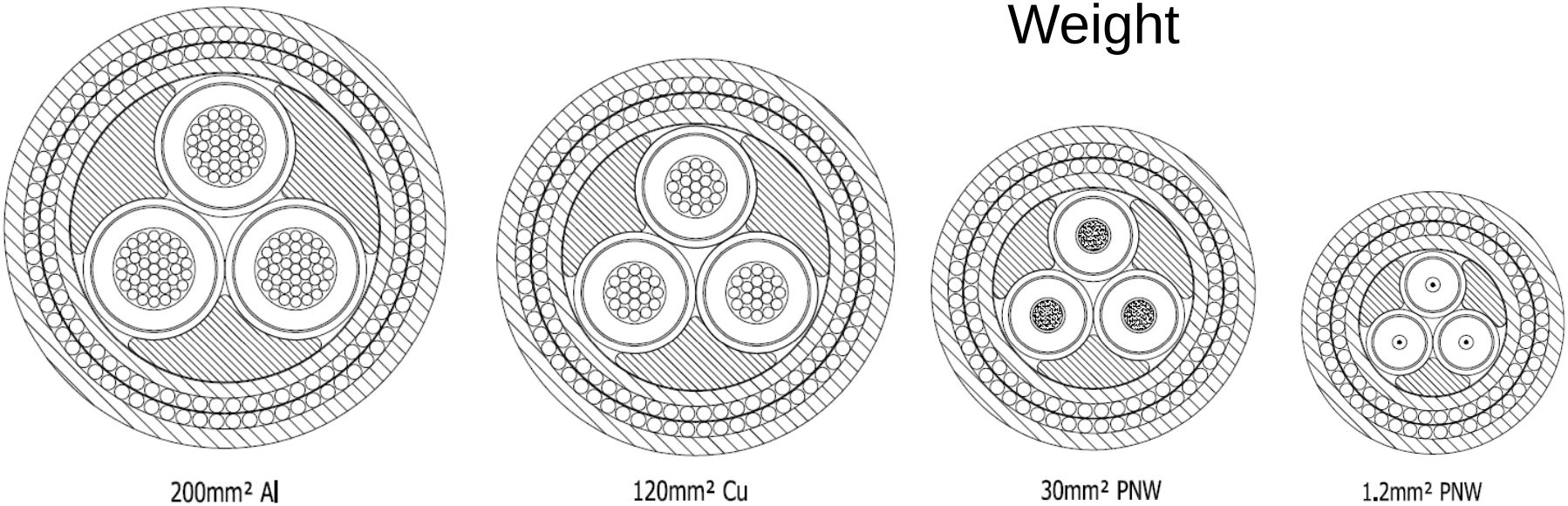
In a classical umbilical which contains double wire armoring, the amount of steel has to be significantly increased to limit conductor strain, for ever increasing water depth.

This tensile limit is governed by the strain on the conductor.

With a PNU conductor the effect of strain may not impose such limitations

Comparison of Power Umbilicals

Weight



Total weight of product for variation of length

length	Total product weight in Tonnes			
10 miles	375	352	233	186
20 miles	750	705	466	373
30 miles	1125	1057	700	560

Electrical Performance

	120mm² Cu		30mm² PNU	
Distance miles	Volt drop %	Power MW	Volt drop %	Power MW
10	10	3.0	10	3.2
20	10	1.2	10	1.3
30	10	0.6	10	0.65

Operating voltage set at 11kV

With the reduction in cable size the Inductance decreases

More power could be delivered, however the electrical stress on the insulation has not been considered, and will increase with smaller conductor

Installation Vessels

For The Deep Blue	120mm^2 Cu	30mm^2 PNU
Length Capacity (km)	123 (76 miles)	186 (115 miles)

Increase in length capacity approximately 50% by weight.
Smaller umbilical OD, will also result in a reduction in the allowable bending radius and a reduction in product volume, i.e. easier to handle

Possible Applications

Conditions for which a lightweight umbilical can be favorable

	Umbilical Length	
Water Depth	Short	Long (>30miles)
Shallow	No	Yes To reduce weight
Deep > 3,000’	Yes To reduce top tension	Yes To reduce weight & tension

Conclusions

- Main impact on umbilicals containing large conductors
- By reducing in top tension, allows more tiebacks to host, but clashing may still be a problem
- Increase in length capacity for existing vessels and manufacturing equipment
- More vessels could be considered for installation, due to reduced tensioner size, smaller umbilical volume and greater allowable bending
- Limitations on conductor strain may be reduced
- Potentially more efficient use of electrical power
- Not promising for shallow water, and short step out

Paradigm Change in Electrical Conductors

nanoUmbilical Workshop

Participants:
NanoRidge Materials: Dean Hulsey, Lori Jacob
Rice University: Enrique V. Barrera, Pulickel Ajayan, Padraig Maloney, Yao Zhao, Divya Chakravarthi
Technip, USA: Jim Dailey, Kerri Dawson
Duco, Inc.: David Madden

Acknowledgements: DOE RPSEA, Chevron

Outline

1. Nanocomposites, Approaches and Applications
2. Polymer Nanotube Umbilical: A High Current Density Conductor
3. Motivation and Concerns for a Nanotube Based Conductor
4. Approach to Producing a PNU
5. Test Methods and Parallel Characterization
6. Current Outcomes

Opportunities for Augmenting Composites with Nanotubes

- Low concentrations of nanotubes for matrix enhancement in fiber reinforced laminate composites. (Improvements have been demonstrated)

  Z-axis enhancement, high temperature use, improved toughness.

- Nanotube dispersion in resins and the study of viscosity changes with degree of dispersion for nanotube only composites. (Viscosity Modification)

  Must overcome viscosity increases and dispersion problems.

- Interpenetrating nanotube networks. (Demonstrated)

  Low cost approach that does not require nanotubes to get unentangled.

- Resin formulation for hybrid polymer formation at both low and high nanotube concentrations. (Demonstrated and high conc. underway)

  Fully integrated nanotube composites. (Demonstrated)

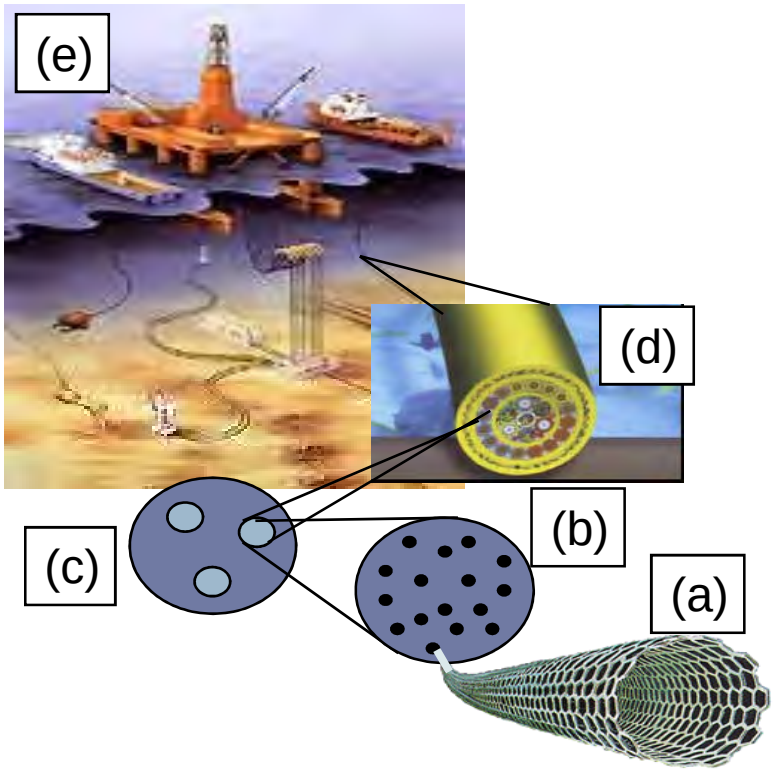
- Cold formable composites that deform like thermoplastics or aluminum.

  A paradigm change in the way we make composites. (Demonstrated)

Polymeric Applications and Drop-off Technologie

1. Electrostatic Discharge Materials (ESD)
2. Lightning Strike Protection
3. Conducting Wires, etc.
4. Multifunctional Composites
5. Reinforced commodity plastics

Polymer Nanotube Umbilical



The PNU is a polymer-nanotube wire that can carry high power to the sea floor.

(a) A SWCNT as the conducting species for the conductor wiring,

(b) Cross-section of a Polymer-nanotube Umbilical (PNU) where nanotubes are dispersed in a polymer,

(c) Cross-section for a three phase power cable,

(d) The umbilical cable that provides power lines to the seafloor, and

(e) The offshore Platform and subsea system.

Team: Rice University, NanoRidge Materials, Inc., Technip, USA and DUCO, Inc. (all are Houston based institutions)

Producing a Conducting Wire or Fiber

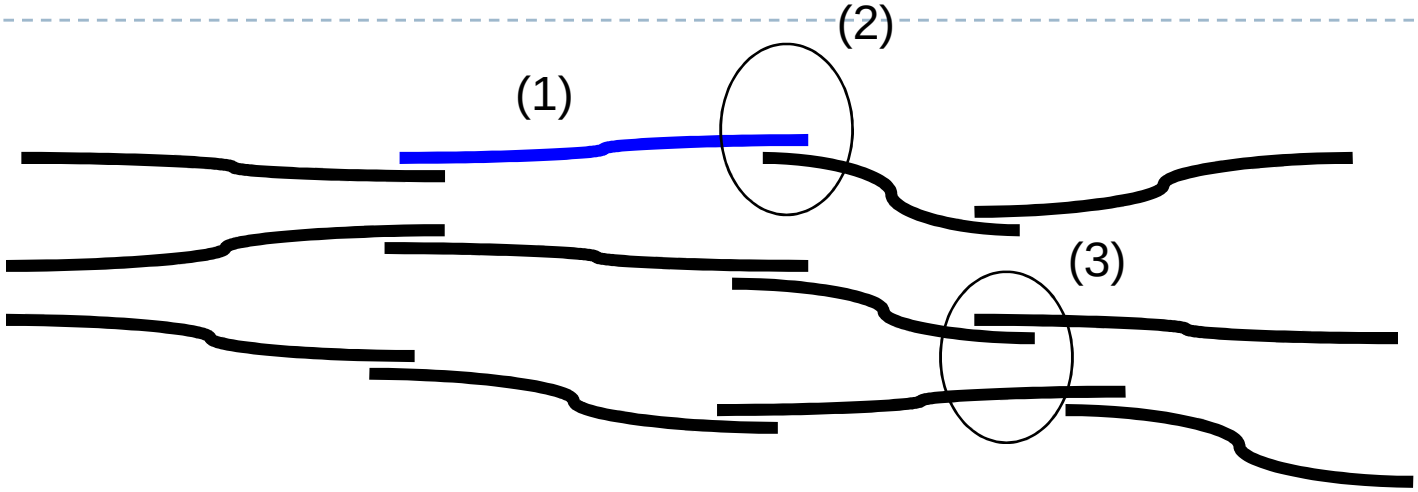
Think about a 50K Tow of fibers and how impressive it is to bring together 50,000 individual fibers.

Consider a 10 wt.% SWNT loading in a polymer which would corresponds to about 300,000,000 individual nanotubes brought together in the polymer

-a 300,000K or 300M Tow product.

A large number of nanotubes produces numerous pathways for electrical conduction.

Directed Nanotube Network (DNN)



A schematic depicting a network of (1) m-SWCNTs that are arranged to promote maximum electrical conduction. The network is made up of (2) connected nanotubes that provide for *ballistic transport* along the nanotube length and *resonant quantum tunneling* from one nanotube to the other. Gap distances between the various chains prevent electron hopping from one pathway to the next. m-SWCNTs may vary in length but the (3) connections will be optimized for low contact resistance.

Nanotubes are nanometers (1.4nm) in diameter and microns in length.
Electrical conduction is as high to better than copper.
Mechanical properties include: UTS: ~50-150GPa/Elastic Modulus: 1 TPa

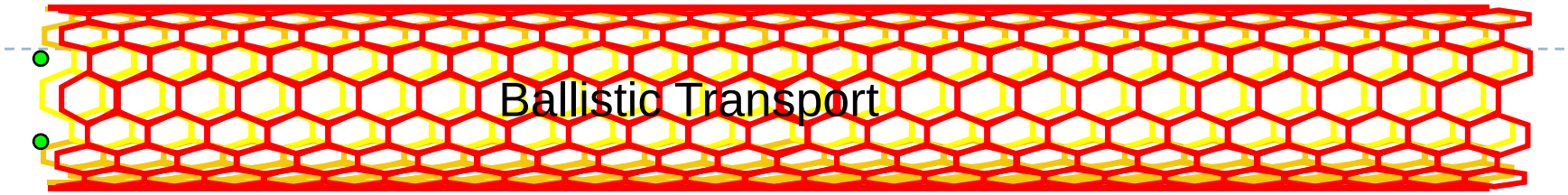
Nanotube Conductivity

http://www.nano.gov/html/news/SpecialPapers/Nanotubes%20For%20Power%20Transmission%20Line%20MaterialsA.htm.
This reference cites the following:

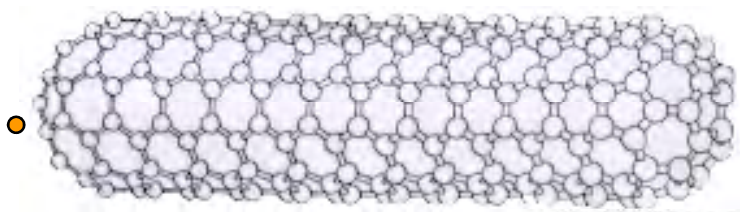
"This high conductivity derives from the highly efficient transmission of electrons down the individual tubes acting as quantum wave guides in one direction, and the efficient resonant quantum tunneling of the electrons from tube to tube as the current passes down the fiber."

Several researchers have demonstrated that one single wall carbon nanotube can carry currents up to **20 microamperes**.

Electron Transport Mechanisms

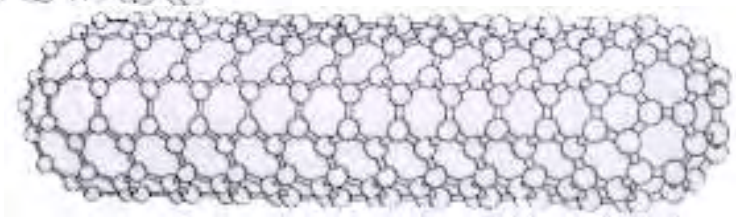


Ballistic conduction allows electrons to flow through the material without collisions. The collisions cause the electrons to slow down, and cause the material to heat, effectively creating resistance in the material.



Transport

Hopping

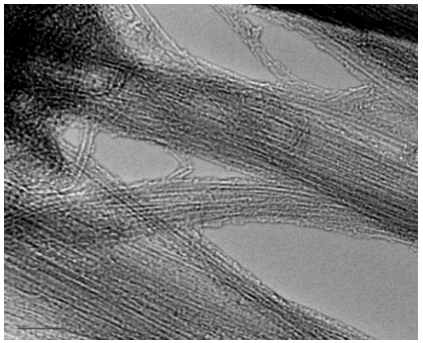


Hopping conduction allows electrons to jump from one nanotube to another. Short contact lengths limit electrons from jumping back and forth.

To maximize conduction, Metallic Nanotubes are needed.

Alper Buldum and Jian Ping Lu, Phys. Rev. B 63, 161403 R (2001).

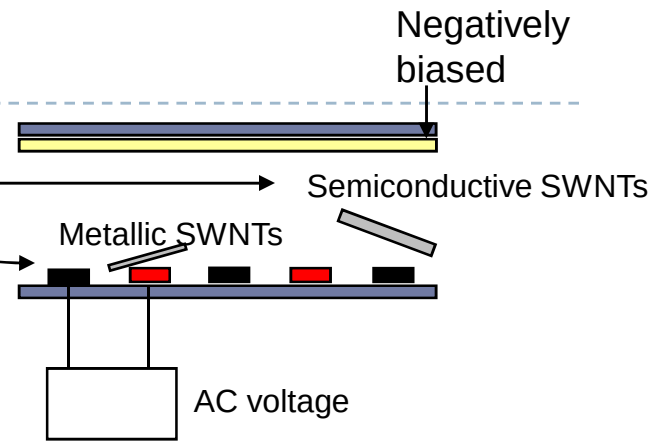
Process Schematic

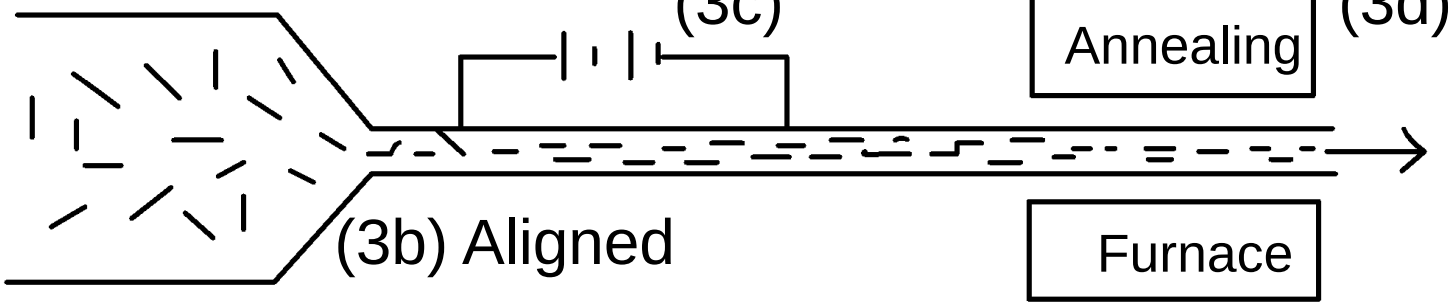


(1)

Semiconductors
Metallic

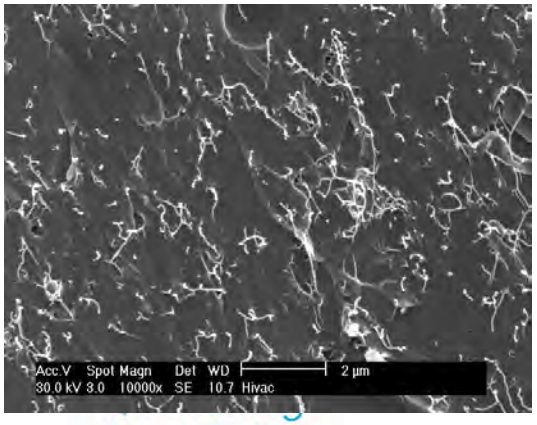
(2)

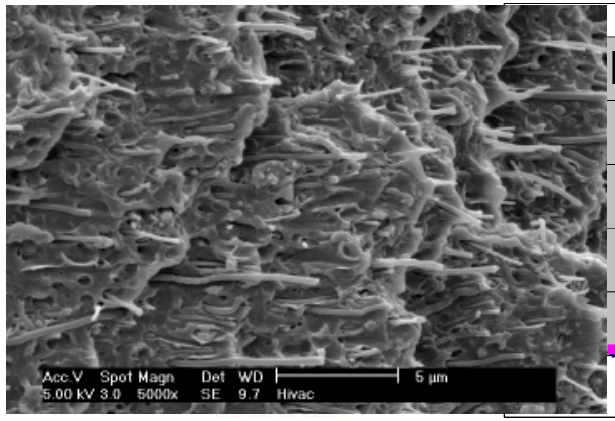


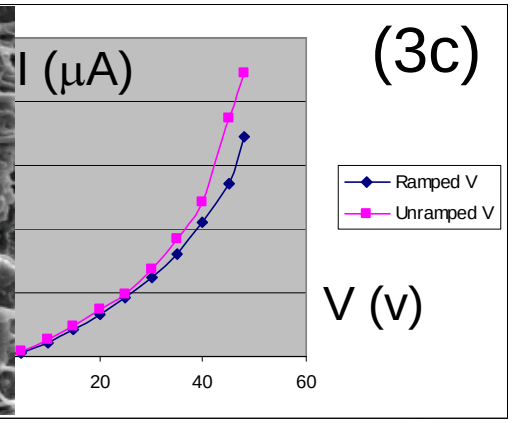


(3a)

(3b) Aligned







Taking a Similar Approach

Self-sorting of Metallic Carbon Nanotubes for High Performance Large Area Low Cost Transparent Electrodes

Zhenan Bao, Department of Chemical Engineering, Stanford University

"The use of carbon nanotubes (CNT) for transparent conducting electrodes in photovoltaic applications.
In order to decrease the sheet resistance, both the electronic properties of the CNTs – namely the tube conductivity and tube-to-tube contact resistance – and the sheet morphology have to be controlled.

Reach this target through the development of solution-based processes to simultaneously separate metal from semiconductor nanotubes using specific surface functional groups (such as amino- and phenyl-silanes on SiO_2 substrates) and control the alignment of the CNTs into bundles during spin-coating deposition.

CNT doping methods are also being investigated to further improve the sheet conductivity.

http://gcep.stanford.edu/research/factsheets/metallicnanotubes.html

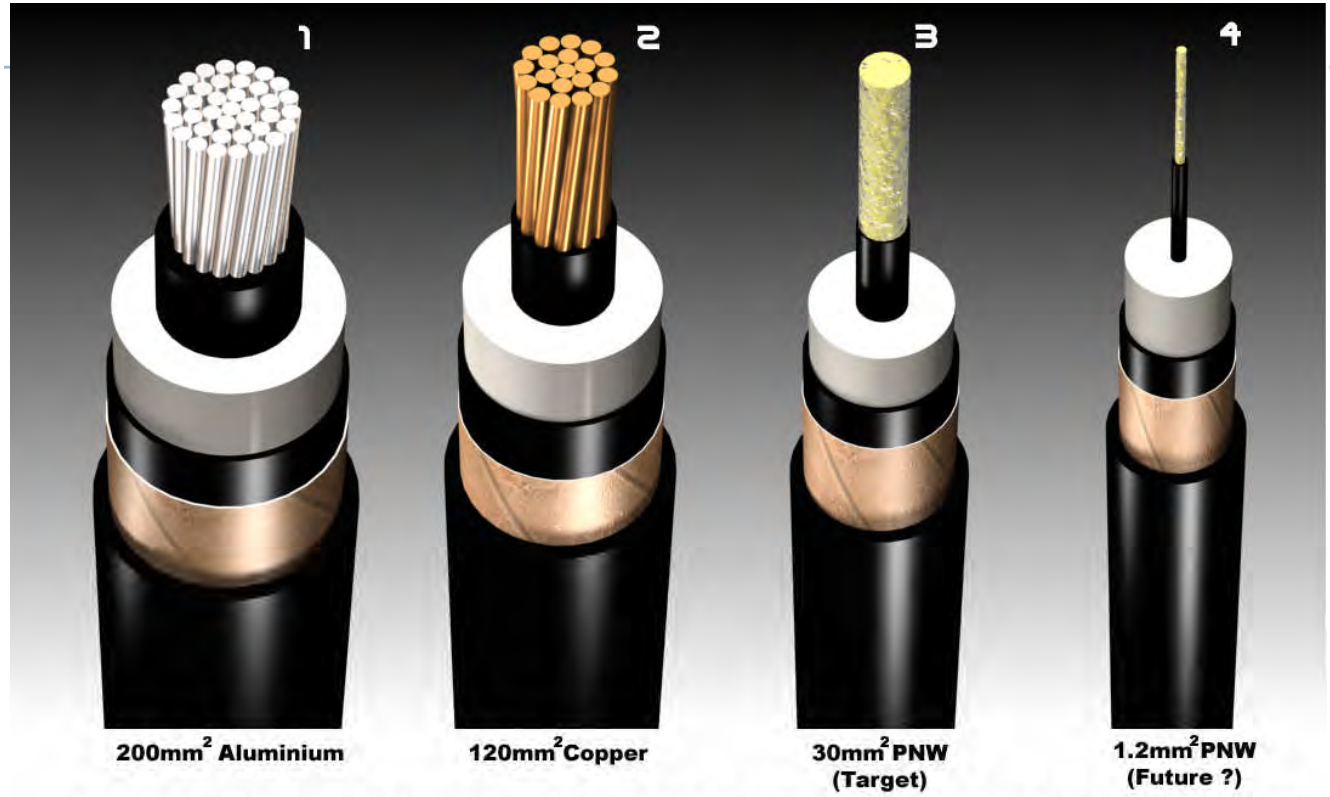
Deliverables

(1) Bridge the gap between engineering science and manufacturing technology to produce a piece of wire.
The wire conductor will be a polymer-Nanotube composite that is half the diameter of a Cu conductor that can carry 500 amps at the same voltage used for the Cu conductor.

(2) Enable engineering aspects of the wire such as crimping, terminations, splicing, and augmentation.

(3) Develop as a low cost conductor with a broad range of uses.

PNU compared to Cu Wire & Cu Stranded Wire



SCREENED POWER CABLES WITH 12/20kV XLPE INSULATION

Overall objective is to design, build and test an engineering prototype of a working ultra-high conductivity "wire" that could in later stages be incorporated into an umbilical exceeding 100 miles in length and called upon to deliver up to 10 MW at up to 36 kV with an operating envelop ranging from -1 to 121ºC (~ 30 – 250ºF) and pressure from
0 to 31.03 MPa (0 to 4500 psi).

Picture compliments of Dave Madden

Concerns

1. Starting purity plays a role.
2. Obtaining separated nanotubes.
3. Level of disentanglement plays a role.
4. Nanotube type is important for two reasons.
   - Probabality of metallic to metallic plays a role.
   - Nanotube to Nanotube contact is important.
   - (S to M (10^0), S to S (10^1), M to M (10^3)
5. Properties produced in the laboratory are not what can be produced in manufacturing.
   - Ropes vs. single nanotubes plays a role.
   - Polymer between the nanotubes plays a role.
     - Wire diameter plays a role.
5. Conditions of the electric fields play a role.
6. Final annealing plays a role.

Improving Percentage of Metallic Nanotubes

(2) Higher percentage m-SWNTs ensures similar type NT-NT contacts. Current nanotube compositions have some metallic to semiconductor contacts (not optimal contacts).

With unseparated nanotubes:

First nanotube is metallic	(1/3 chance is metallic)
Second nanotube is metallic	(1/3 chance is metallic)
Chance of metallic to metallic:	(1/9)

With current sorted nanotubes:

First nanotube is metallic	(2/3 chance is metallic)
Second nanotube is metallic	(2/3 chance is metallic)
Chance of metallic	(4/9 chance, improved by 2)

With proposed enhancement:

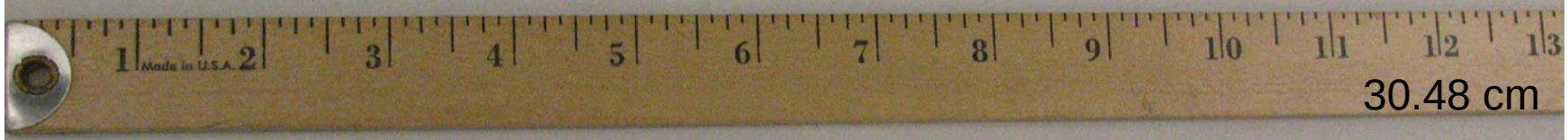
First nanotube is metallic	(8/9 chance is metallic)
Second nanotube is metallic	(8/9 chance is metallic
Chance of metallic	(64/81 chance, improved by 7)

Resulting Diameters

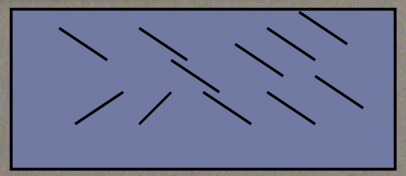
PE w/10 wt% SWNTs/Processed by melt spinning.

Various diameters have been produced with smaller diameters being more optimal at this time.

Smaller diameters lead to smaller distance between nanotubes.

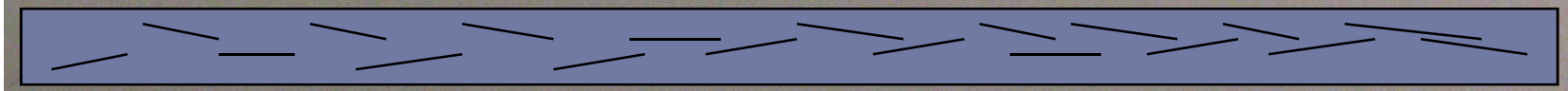


30.48 cm



Explanation for thinner wire, better conductivity

Keep the same volume, 1/2 diameter, ¼ cross section area, 4 x length (a cost savi



Better alignment in uniaxial direction

The Role of Concentration and Shear

High Mechanical Performance Composite Conductor: Multi-Walled Carbon Nanotube Sheet/Bismaleimide Nanocomposites By Qunfeng Cheng, Jianwen Bao, JinGyu Park, Zhiyong Liang,* Chuck Zhang, and Ben Wang, Adv. Funct. Mater. 2009, 19, 1–7.

"Applying mechanical stretching and prepregging (pre-resin impregnation) on initially randomly dispersed, commercially available sheets of millimeter-long MWNTs leads to substantial alignment enhancement, good dispersion, and high packing density of nanotubes".
"The nanocomposites demonstrate high electrical conductivity of 5 500 S cm^{-1} along the alignment direction". Concentration of nanotubes was 60 wt% MWNTs.

High concentrations and shear can enhance conduction conditions.

Electric Field Specifications

A review and analysis of electrical percolation in carbon nanotube polymer composites Wolfgang Bauhofer, Josef Z. Kovacs,
Composite Science and Technology, 69 (2009) 1486-1498.

Review of 121 papers on electrical properties.
Results from the review:
(1) Dispersion is very important.
(2) Entanglements reduce conductivity (up to 50 times (MWNTs))
(3) Electric fields align nanotubes and enhance attractive forces between nanotubes.

400 x 10^{-6}m (0.4 mm) separation between electrodes for electric field use.

Electric Field Alignment

Electric-field assisted assembly and alignment of metallic nanowires
Peter A. Smith, Christopher D. Nordquist, Thomas N. Jackson, and Theresa S. Mayera, *Benjamin R. Martin, Jeremiah Mbindyo, and Thomas E. Mallouk*

"This letter describes an electric-field assisted assembly technique used to position individual nanowires suspended in a dielectric medium between two electrodes defined lithographically on a SiO2 substrate. During the assembly process, the forces that induce alignment are a result of nanowire polarization in the applied alternating electric field. This alignment approach has facilitated rapid electrical characterization of 350- and 70-nm-diameter Au nanowires, which had room-temperature resistivities of approximately 2.9 and 4.5 x 10- 6 ohm cm".

(5 micron wide electrodes)

http://research.chem.psu.edu/mallouk/articles/APL01399.pdf

Electric Field Alignment

Aligned Single-Wall Carbon Nanotube Polymer Composites Using an Electric Field CHEOL PARK, JOHN WILKINSON, SUMANTH BANDA, ZOUBEIDA OUNAIES, KRISTOPHER E. WISE, GODFREY SAUTI, PETER T. LILLEHEI, JOYCELYN S. HARRISON, Journal of Polymer Science: Part B: Polymer Physics, 44 (2006) 1751-1762.

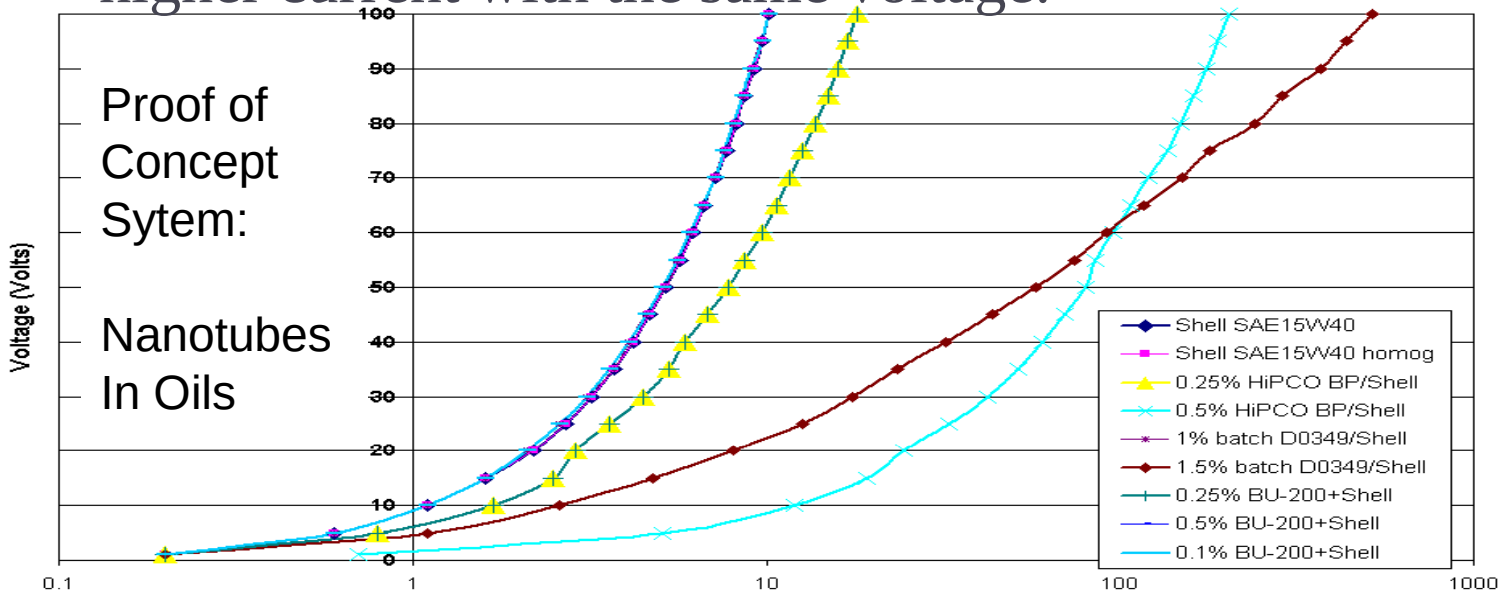
Use of electric fields 0.03 wt% Hipco.

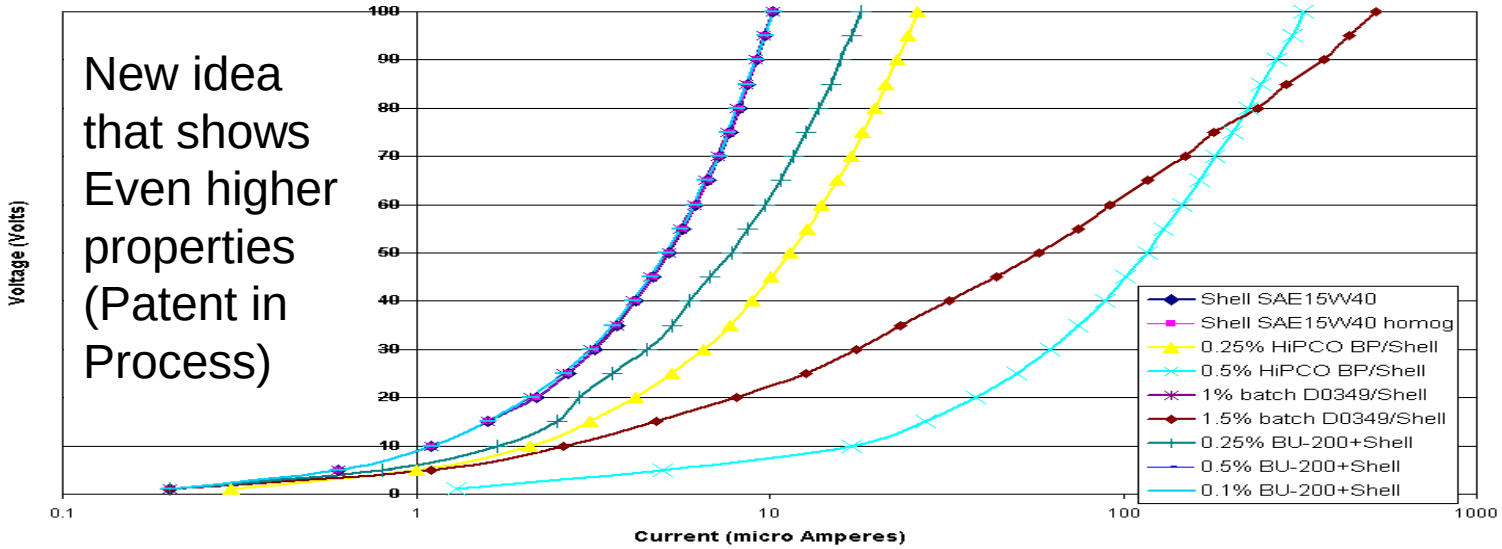
Electrodes placed at a separation distance of 2.3 mm. In the electric field for 10 minutes. 10^{-6} S/cm

Self-Assembled Linear Bundles of Single Wall Carbon Nanotubes and Their Alignment and Deposition as a Film in a dc Field Prashant V. Kamat, K. George Thomas, Said Barazzouk, G. Girishkumar, K. Vinodgopal, and Dan Meisel†.
5 mm apart.
"When a dc voltage of ~40 V was applied, we observed a slow movement of carbon nanotubes from the suspension toward the positive electrode".

Proven Increase in Electrical Conductivity

Voltage vs. Current: Curves with nanotubes achieve higher current with the same voltage.





Tunneling

Dominant role of tunneling resistance in the electrical conductivity of carbon nanotube–based composites Chunyu Li, Erik T. Thostenson, and Tsu-Wei Chou,
Applied Physics Lett. 91 (2007) 223114-1 to 223114-3.

Maximum tunneling distance is found to be 1.8 nm.

“Electrical conductivities of composites with in plane random distributions of carbon nanotubes follow the scaling law and the critical exponent depends on the level of contact resistance”.

“It is also noted that the extrapolation of the EC of CNT networks without insulating layers at 100% content gives about 7.2 - 10^5 S / m, which is very close to the conductivity of 10^6 S / m of individual CNTs we used”.

Conduct NT-NT Study/Improve NT-NT Connection

Three Approaches: (1) Zyvex manipulation
(2) Ames Interdigitized Sample
(3) Use of Focused Ion Beam Equipment
(4) Doping

Use of Focused Ion Beam Equipment

IPICyT in San Luis Potoci, Mexico has equipment for conducting high sensitivity nanotube manipulation.

With this equipment we can imagine at the nanoscale, move nanotubes around, and create contact conditions for measuring electrical conductivity (NT-NT contact).

Experiments are being conducted to achieve samples of several nanotube conditions.

Nano-Manipulator Approach to Transport Measurement: Initial work

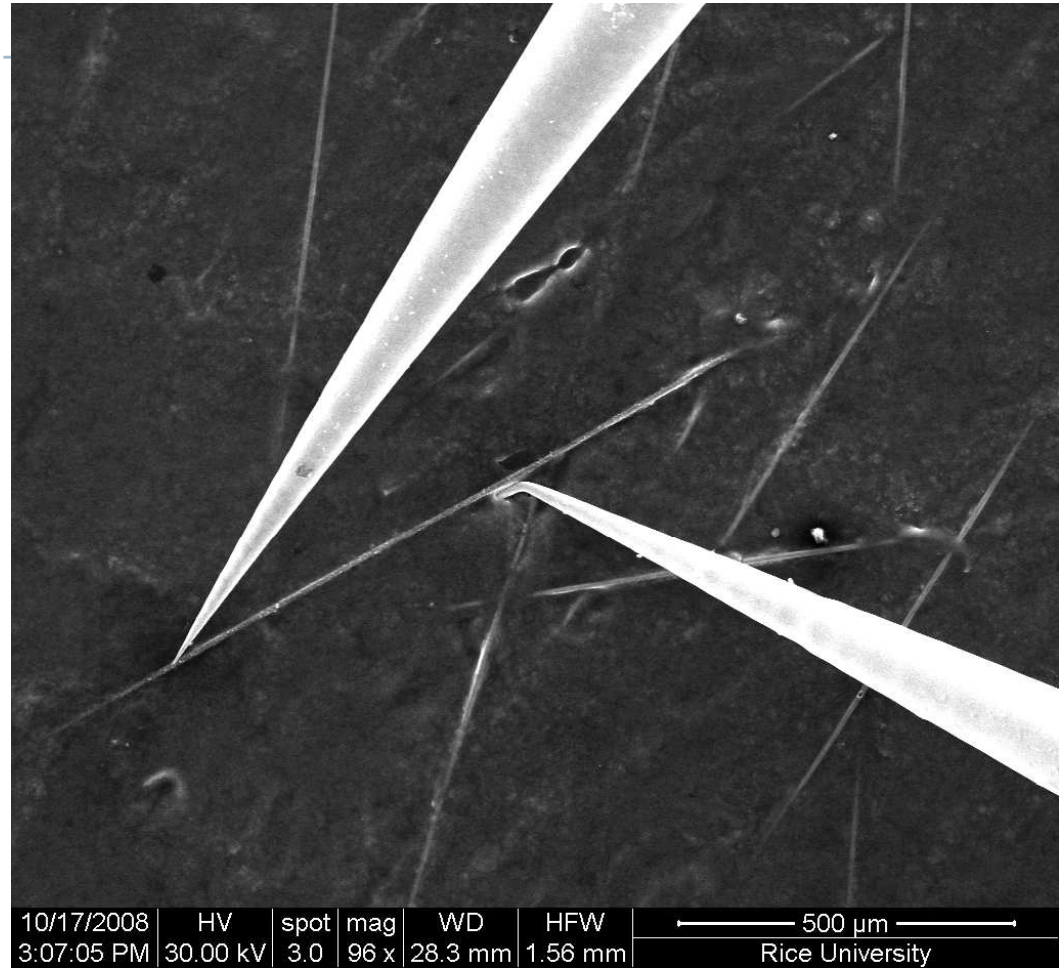
Currently a two-probe contact system is used where the nanotube is isolated from the substrate surface.

Options for a four point contact arrangement are available depending on the space around the four contacts.

Consistency of contact to the nanotube must be achieved and optimized for best contact conditions.

Properties as a function of temperature will also be measured.

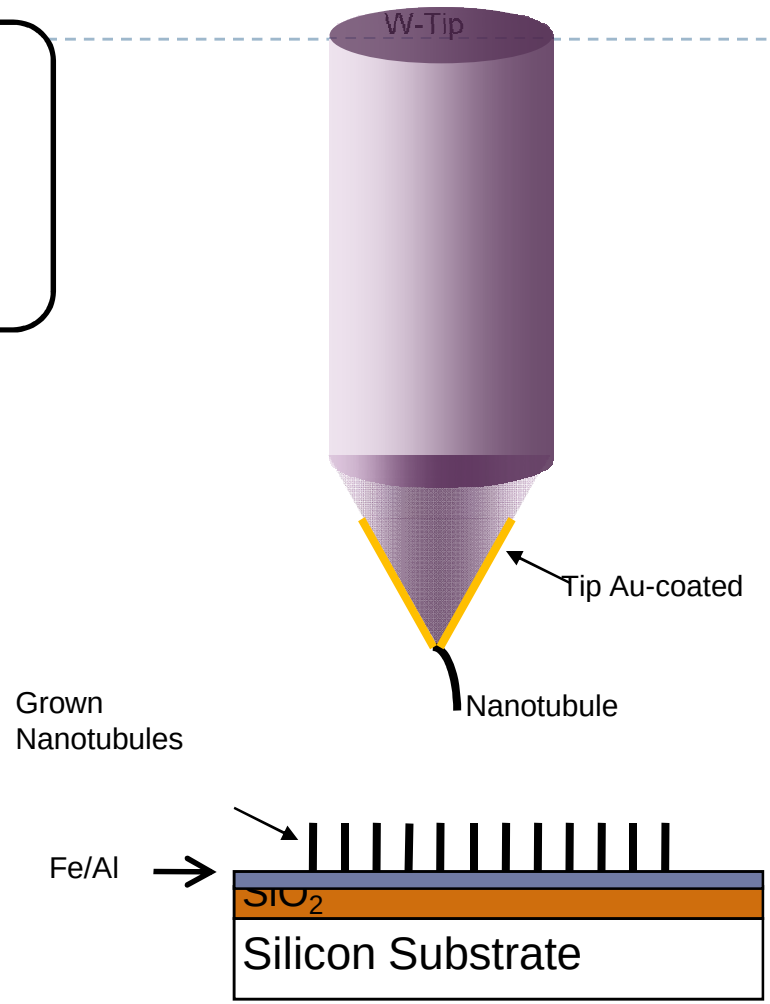
Nanotube manipulation is necessary in order to manipulate the contact conditions.



- Instrument is available and inexpensive.
-(MWCNT: 105 µAmps, 9.52 kohms (clamping). Difficult to manipulate CNT in matrix.
-50 nm movement resolution. SEM resolution - large working distance.

Nano-Manipulator Approach to Transport Measurement: Solution

GOAL: Measure Tunneling Transport b/t nanotubes In a polymer-matrix.



Process:

Tip

- Coat Zyvex Tips w/ Thin-Layer Au.
- Attach Nanotubule to Zyvex Tip.

Substrate

- Grow/Deposit SiO_2 on Si-subst.
- Deposit Fe/Al Film on SiO_2.
- Grow CNT (DW) on Fe-catalyst.
- Vary CNT length.
- Pattern substrate.
- Wet grown-CNTs w/ polymer matrix.

Conductivity of SWNT Networks

Electrical Conductivity of Single-Walled Carbon Nanotube Networks
P. N. Nirmalraj, P. E. Lyons, S. De, J. N. Coleman, and J. J. Boland, Nano Le (2009) 3890-3895.

“Transport in single-walled carbon nanotube networks is shown to be dominated by resistance at network junctions which scale with the size of the interconnecting bundles”.

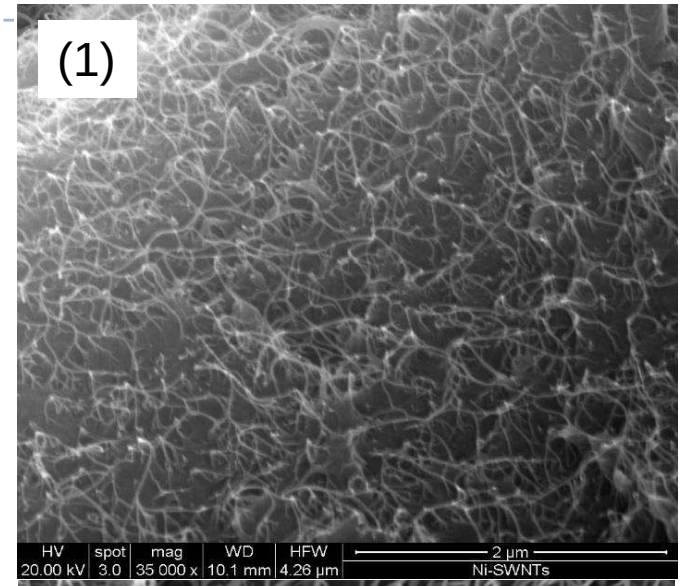
“Acid treatments that dope the individual nanotubes produce a dramatic reductionin junction resistance.

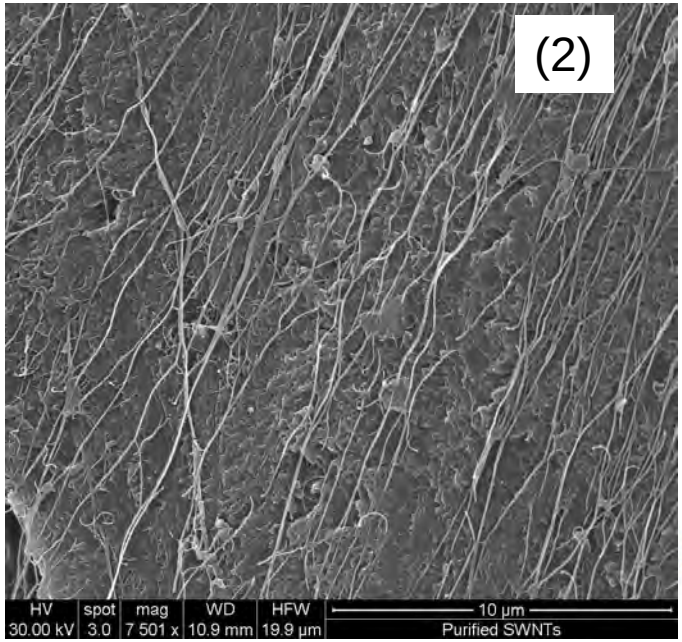
Smallest resistances occurs between individual nanotubes.

Disperse m-SWNTs

The Winey method for dispersion:
A version of the Incipient Wetting method where the following is used:

1) SWNTs are dispersed in Dichlorobenzene and sonicated. 2) After 3 hours, the temperature of the SWNT + DCB is raised to 110C. In a different beaker MDPE is dissolved in DCB at 110C. 3) The DCB + MDPE solution is added to the SWNT dispersion. 4) The mixture is placed in a ice bath and sonicated till the temperature reached below 70C. 5) The mixture is then vacuum filtered and dried.

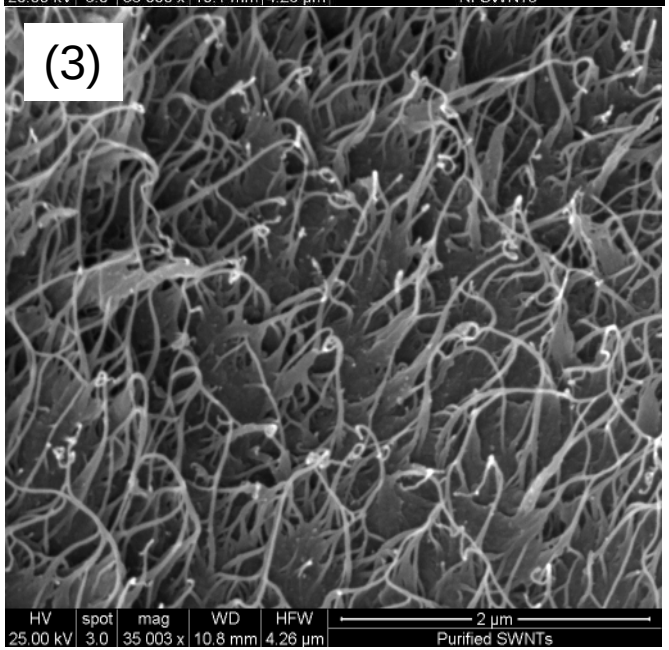




(1) After Winey Method.

(2) After electric Field applied.

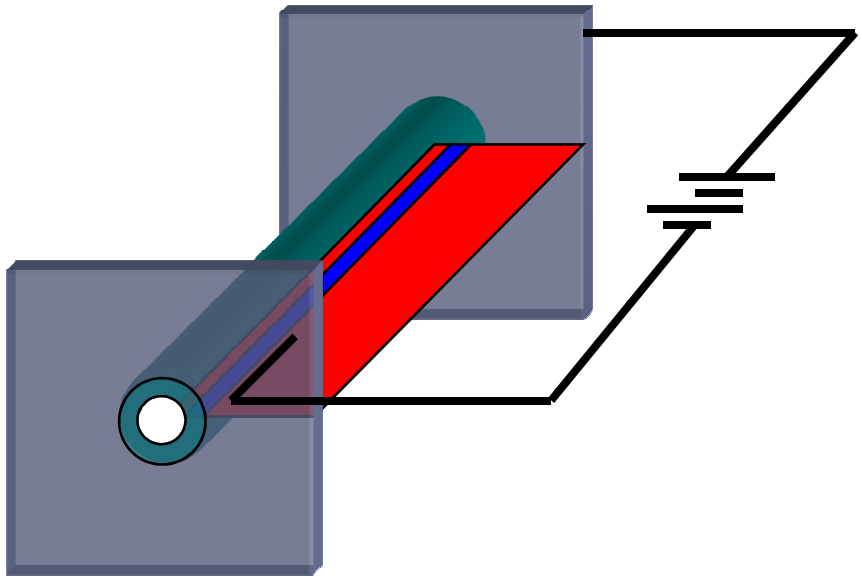
(3) After electric Field applied.



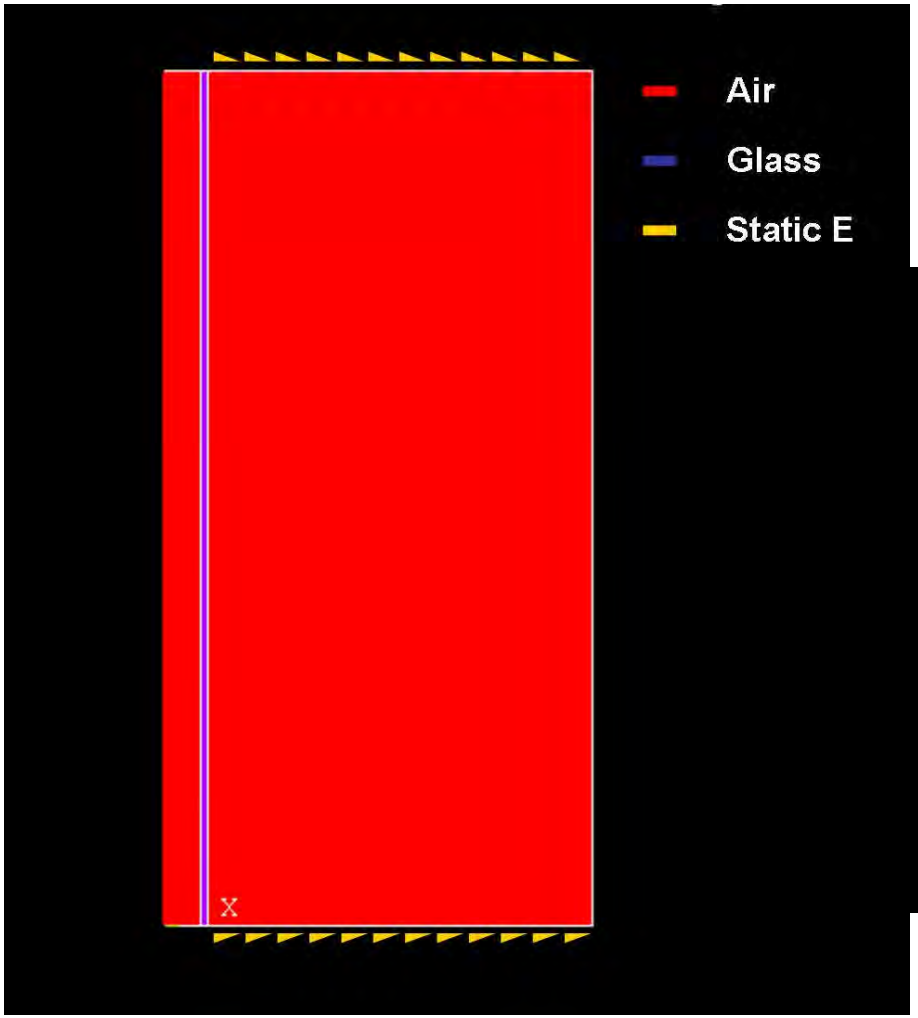
Implement Electric Fields

Design of an Electric Field Fixture:

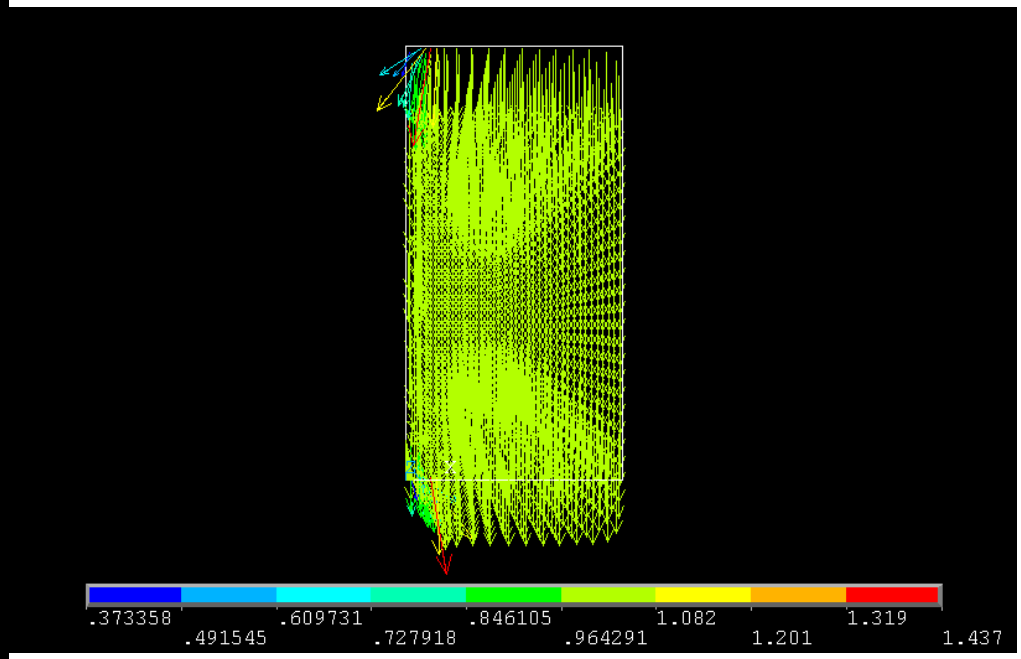
1. Separated parallel plates with a hole in the middle so the PNU can go through.
2. A tube is placed in the holes so that a heating element can be put around the wire.



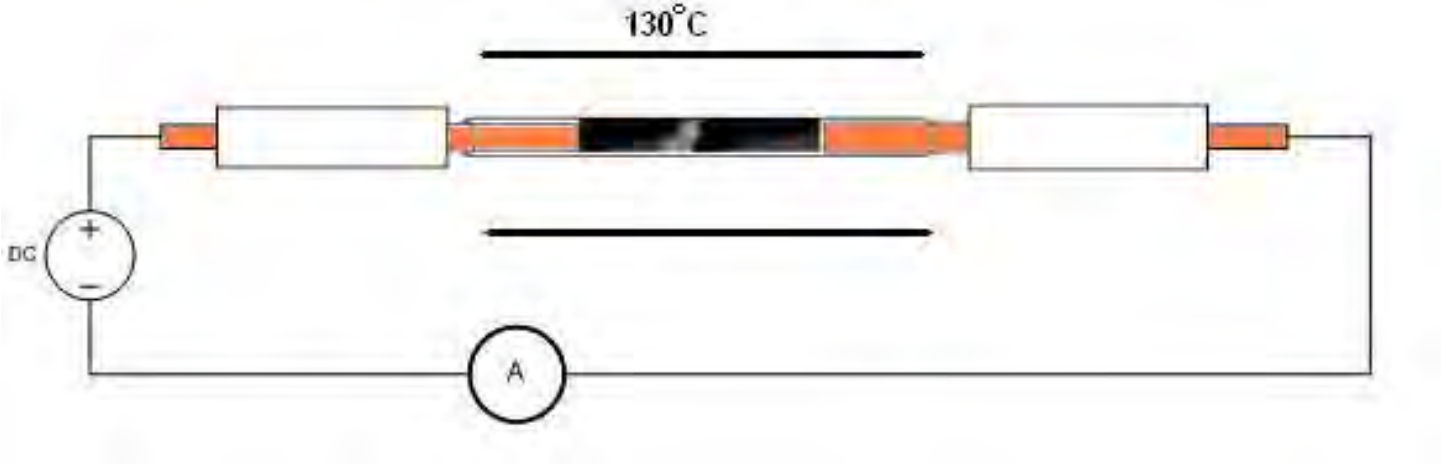
Finite element analysis



Finite Element Analysis (FEA) shows a uniform field with minor disruption at the plats around the holes.



Current method for implementing the electric field



- 4 samples (MDPE + 10 wt% SWeNTs) were tested.
- Samples required 4 ~ 5 rounds of conditioning, before it starts conducting well.
- The best samples carried a current of close to 16 amps for 2 V.
- The distance between the leads for the best sample is close to 0.7 cm.
- Specific resistivity was 2.1 * 10^{-2} ohms / sq.cm
- Current samples require conditioning (more than one melting pass).

Example Samples Processed to Date

Composites	Wt% of NTs	Processing method
MWNTs/HDPE	5%	Dry mixing + Injection
MWNTs/HDPE	10%	Dry mixing + Injection
MWNTs/HDPE	15%	Dry mixing + Injection
MWNTs/HDPE	20%	Dry mixing + Injection
MWNTs/HDPE	5%	Dry mixing + Haake extrusion
MWNTs/HDPE	10%	Dry mixing + Haake extrusion
MWNTs/HDPE	15%	Dry mixing + Haake extrusion
MWNTs/HDPE	20%	Dry mixing + Haake extrusion
MWNTs/HDPE	5%	Incipient wetting + Dry mixing + Haake extrusion
MWNTs/HDPE	10%	Incipient wetting + Dry mixing + Haake extrusion
MWNTs/HDPE	15%	Incipient wetting + Dry mixing + Haake extrusion
MWNTs/HDPE	20%	Incipient wetting + Dry mixing + Haake extrusion
MWNTs/HDPE	5%	Dry mixing + Miniextrusion
MWNTs/HDPE	10%	Dry mixing + Miniextrusion
MWNTs/HDPE	15%	Dry mixing + Miniextrusion
MWNTs/HDPE	20%	Dry mixing + Miniextrusion
MWNTs/HDPE	30%	Dry mixing + Miniextrusion
MWNTs/HDPE	40%	Dry mixing + Miniextrusion
MWNTs/HDPE	50%	Dry mixing + Miniextrusion
MWNTs/HDPE	60%	Dry mixing + Miniextrusion
CG NTs/HDPE	10%	Winney sample + Injection
CG NTs/HDPE	10%	Winnery sample + Miniextrusion
MWNTs/MDPE	5%	Dry mixing + Haake extrusion
MWNTs/MDPE	10%	Dry mixing + Haake extrusion

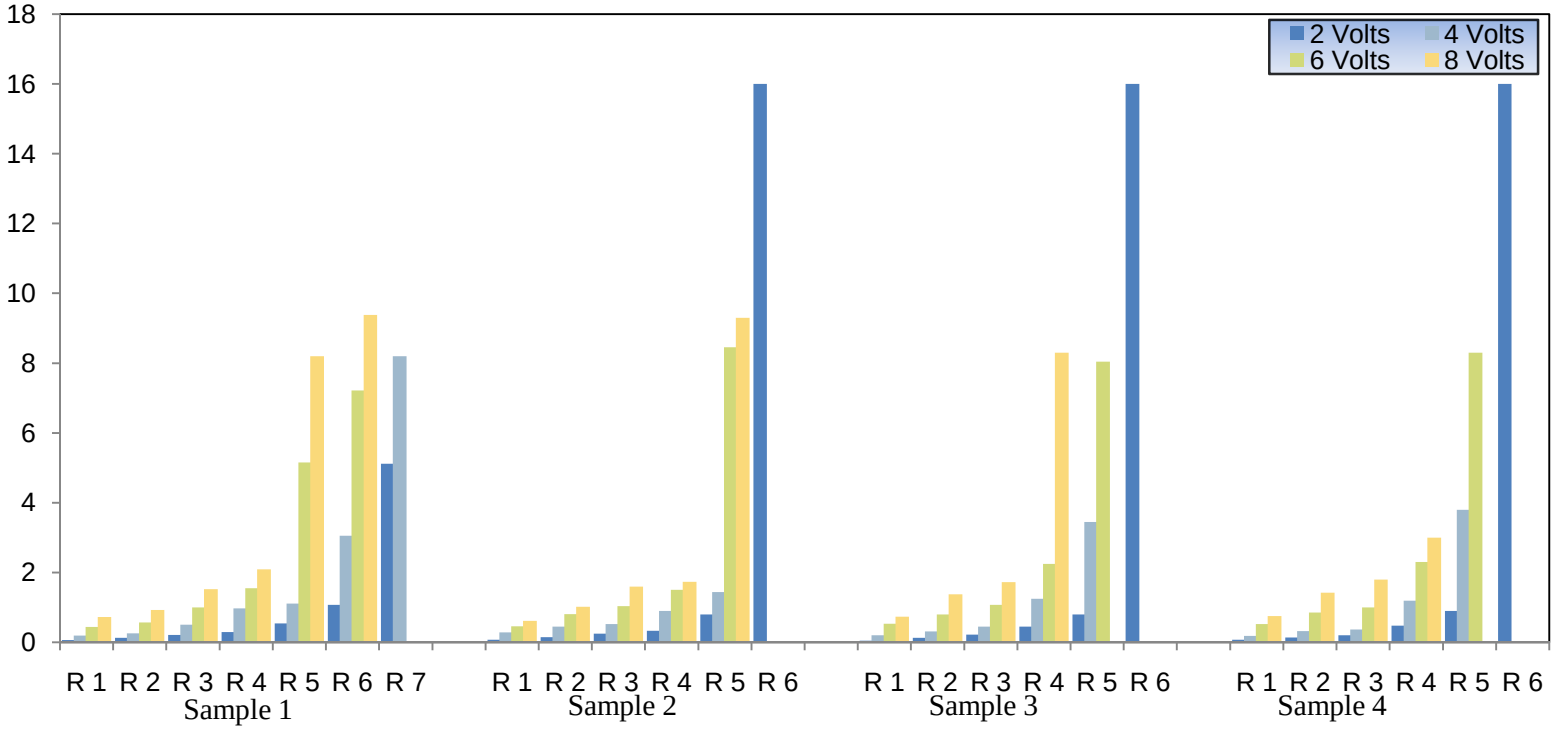
Three melt processing approaches are being used:

- Injection molding (up to 6 grams)
- Mini-extrusion (10 grams)
- Haake extrusion (100 grams).

Wt%s from 5 to 60 are being processed. Typical concentrations are 10 wt%.

Evaluation & Optimization

Target: 500 amps at the same voltage for the copper conductor.
Proposed: (a) Stranded wire (19 strands) or (b) Solid Core wire.
For stranded wire: On average ~26 amps to be carried by each strand.
Current Design and Evaluation: Single strand of SWNTs/PE.



Recent conditions may be limited by available power supply.

Program Outcomes

1. One foot wire conductor produced.
2. High dispersion has been achieved by the “Winey” Method.
3. We have used electric fields and designed a fixture for process manufacturing.
4. We have produced a number of samples using the Dymax sample configuration. Early samples were produced with styrene. A number of samples have been processed by melt spinning.
5. A current carrying capability of 16 amps has been produced
6. where 26 A is needed..

   The sample was limited by the power supply used.

   More optimization is planned.
6. The workshop is being held on Ultra-High Conductivity Conductors.
7. The test wire is being demonstrated at the workshop.

Program Support: DOE RPSEA, Chevron

nanoUmbilical
Workshop

PNU properties at the nanoscale

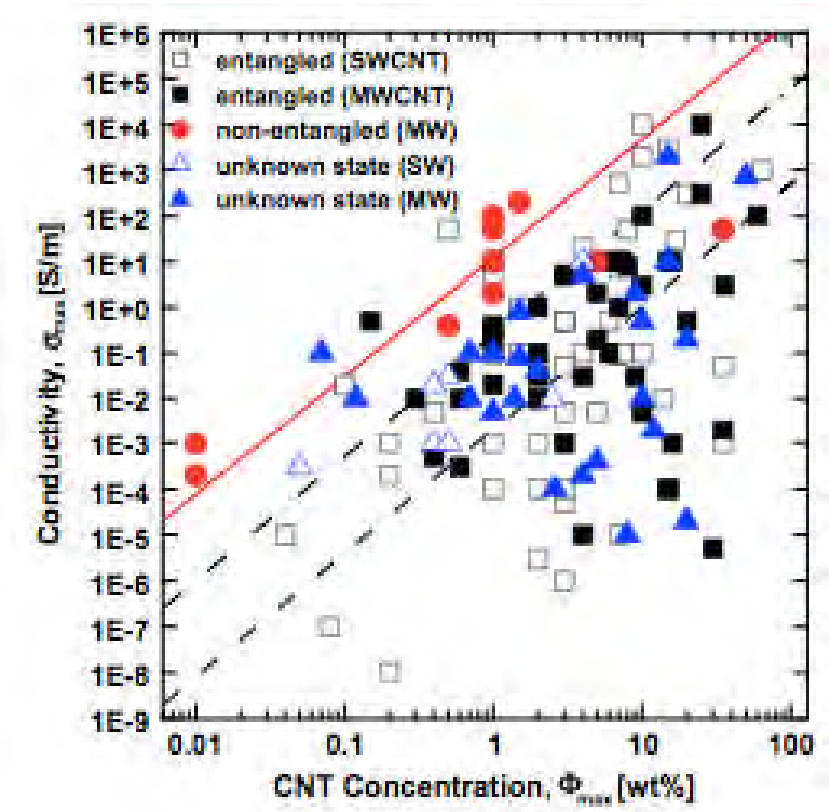
Pádraig G. Moloney, Divya K. Chakravarthi, Yao Zhao, Lori Jacob, Dean Hulsey, Enrique V. Barrera

Agenda

- Introduction – current literature & research
- Selection of nanotubes/m-SWNTs
- Optimizing nanotube-to-nanotube contact
  - Nanoscale - Zyvex nanomanipulator
  - Microscale transport measurement - Interdigitated electrodes
  - Macroscale – Bulk tests in Dymax
  - In polyethylene
  - Doping (Patent in process)
  - Novel processing route (Patent in process)
  - High wt% CNT loading

Introduction

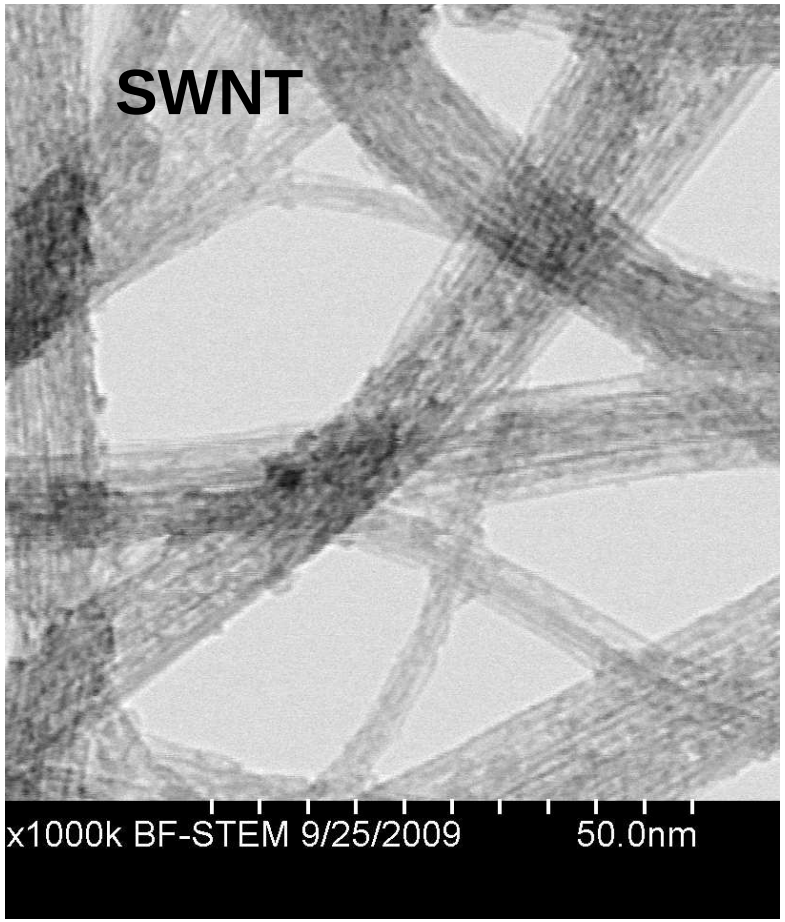
- Current literature & research:
  - $1*10^{-2}$ Ω•cm PMMA 10wt% $SOCl_2$ SWCNT [1]
  - $3*10^{-1}$ Ω•cm PANI 15wt% SWCNT [2]
  - $2*10^{-1}$ Ω•cm PU 15wt% MWCNT [3]

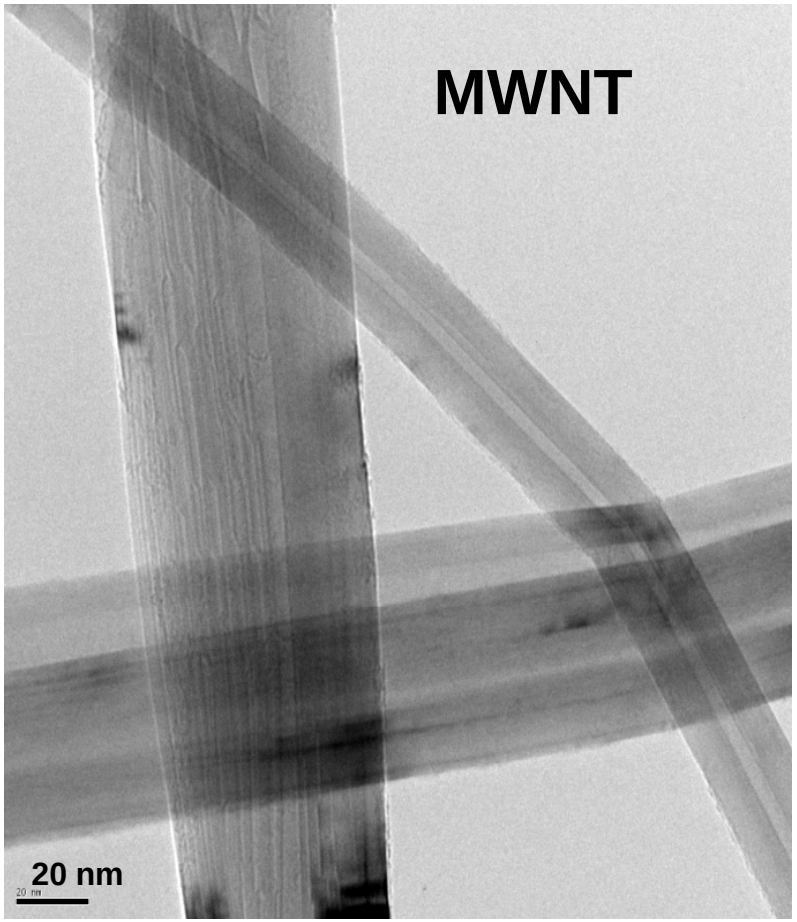


W. Bauhofer, J.Z. Kovacs / Composites Science and Technology 69 (2009) 1486

1. V. Skakalova´ et al. / Synthetic Metals 152 (2005) 349–3520
2. Blanchet et al, Appl. Phys. Lett., Vol. 82, No. 8, 24 February 2003
3. H. Koerner et al. / Polymer 46 (2005) 4405–4420

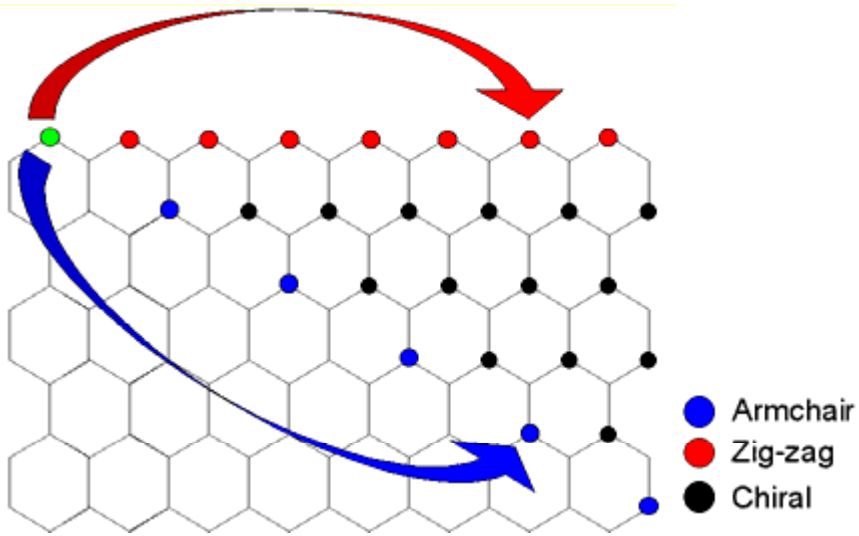
Nanotube Selection: Single & Multi-wall

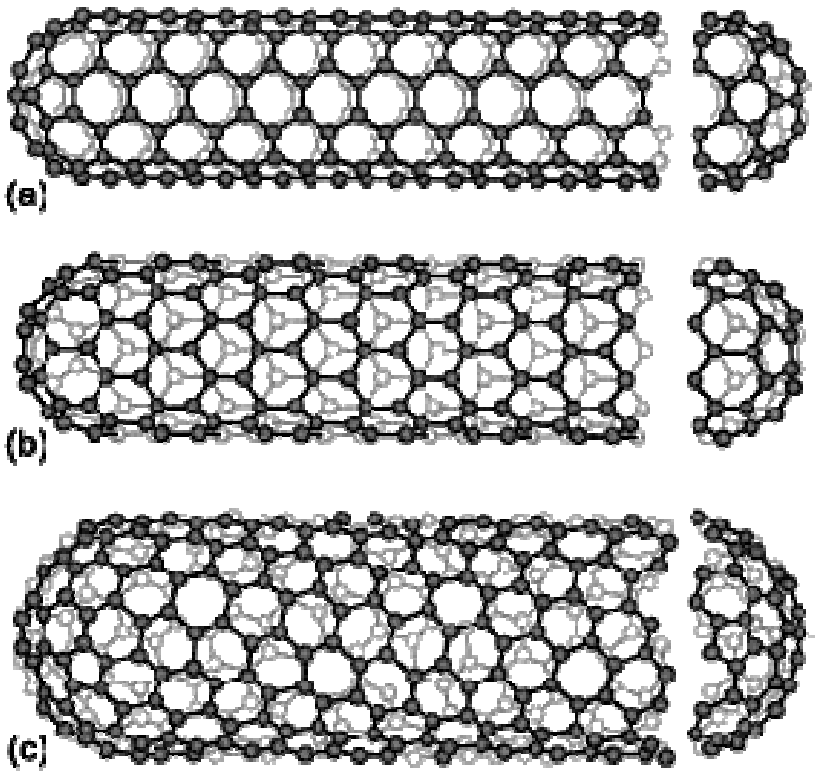




1. © Prof. Alain Rochefort

Single wall carbon nanotubes

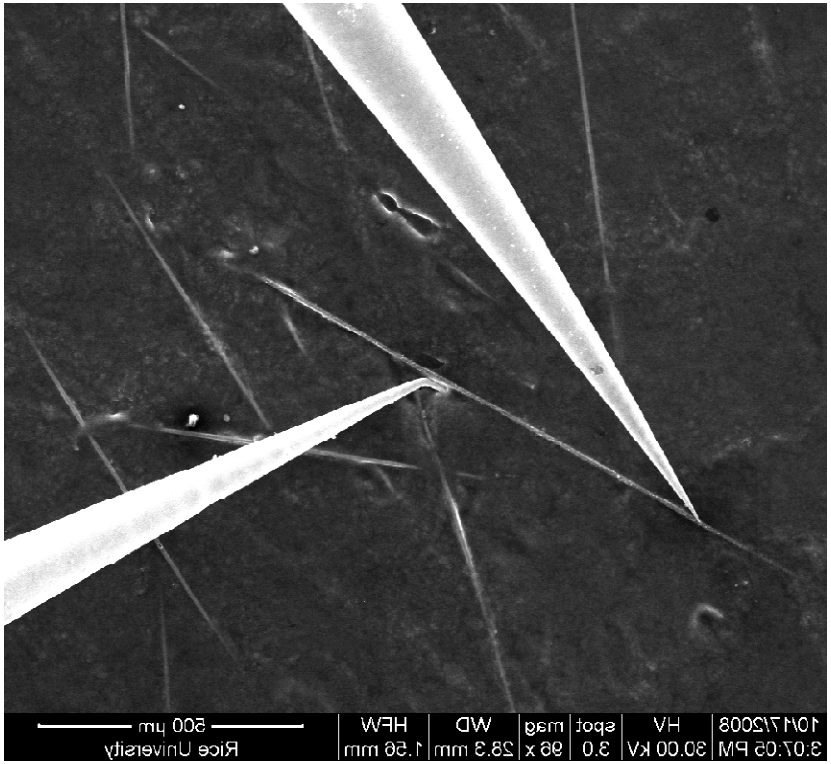


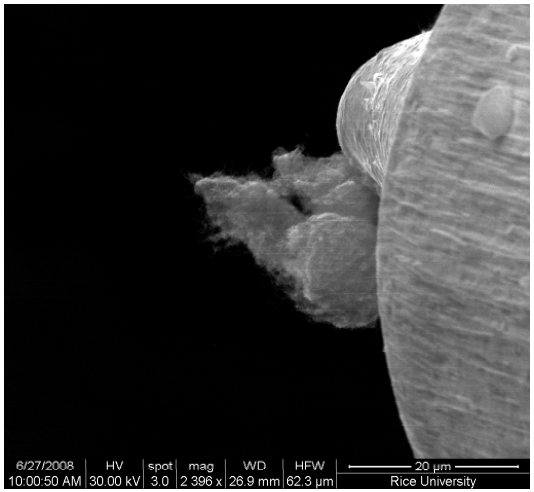


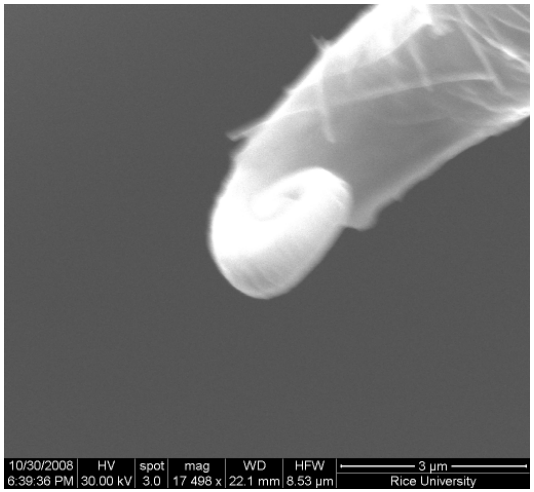
Arm-chair and one-third of zig-zag nanotubes are metallic. This means they have a continuous conduction band.

The remaining two-thirds of the zig-zag nanotubes are semiconductors, meaning that their conduction band has an energy gap which limits the flow of electrons.

Optimizing CNT-CNT Contact: Nanoscale - Zyvex nanomanipulator

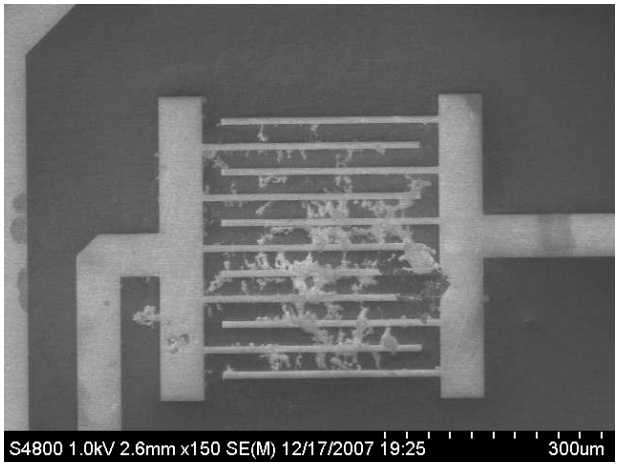


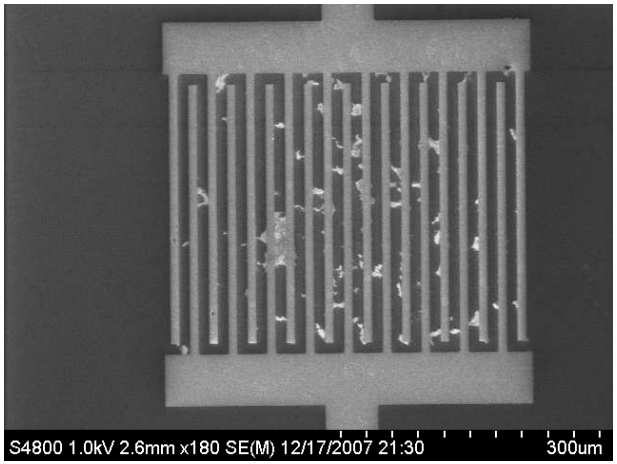




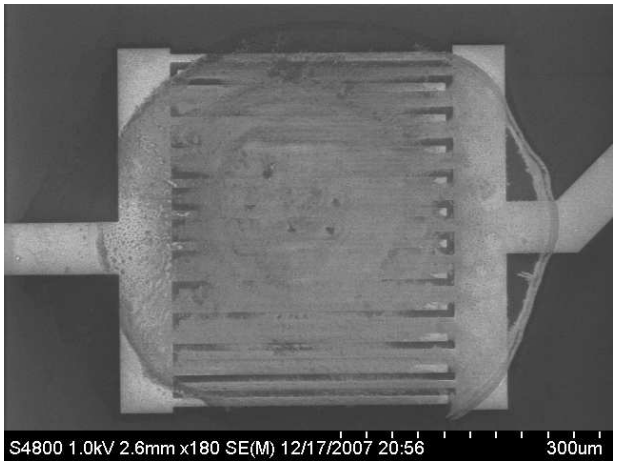
- *Jan – March 2009*
- (Above) MWCNT: 105µAmps, 9.52 KΩ (clamping)
- - Difficult to manipulate CNT in matrix (top right, right)
- - 50 nm movement resolution

Optimizing CNT-CNT Contact: Microscale transport



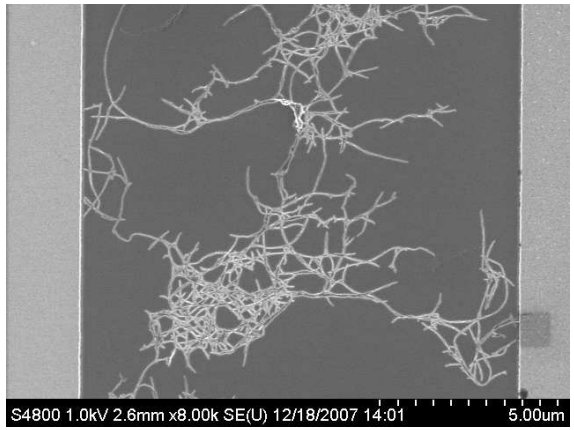


- *Jan – Feb 2009*
- Deposition of CNT and solvent onto interdigitated chip (Ames & Rice U)
- - 7 nL volume deposited - 15mg/mL concentration
- - Control of droplet position, concentration & viscosity (SEM image - right)
- 20 sample matrix, 3 sensor pad each; 60 sensor pads

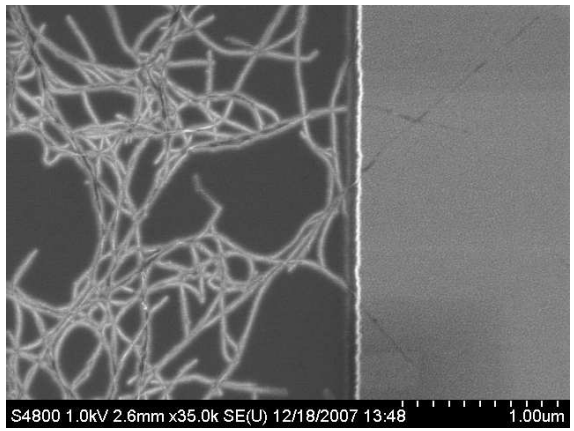


Optimizing CNT-CNT Contact: Microscale transport

- Matched bulk trends
- Favored Laser SWNT and SWeNT CG 100 SWNT
- MWNT, Ag-coated SWNT and other functionalized tubes not as conductive



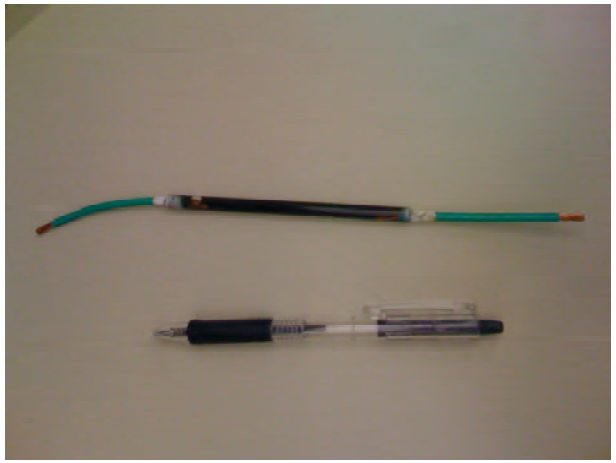
Areas of interest: CNT networks formed

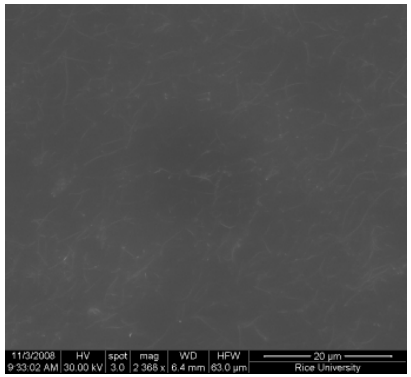


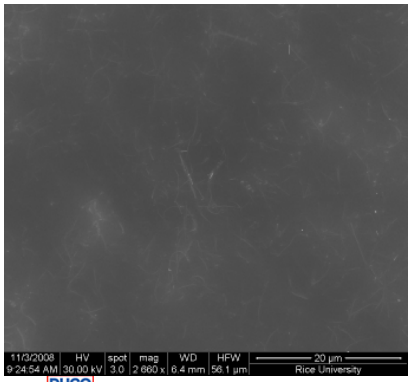
Optimizing CNT-CNT Contact: Bulk transport in Dymax

- *Feb/March 2009*
- SWNT most suitable
- Laser-produced tubes most conductive
- Bulk statistics match trends with microscale work
- Showed initial value of electrical conditioning

Ω•cm	
Dymax Polymer	10^8 +
5.0% Graphite (NanoRidge)	10^5
1.4% Purified HiPco	10^2
Mitsui MWNT	10^1
Laser AQW	10^-1
Cu	10^-8



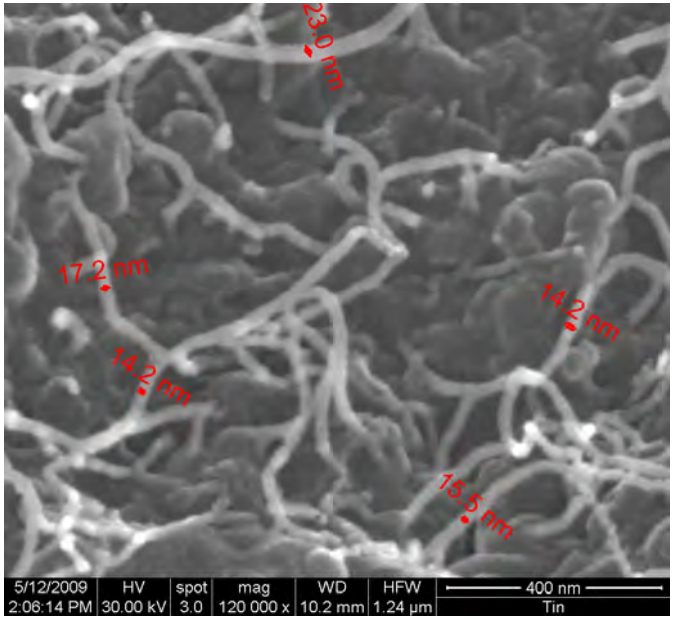




Uncure vs. Cure
Mitsui MWNT

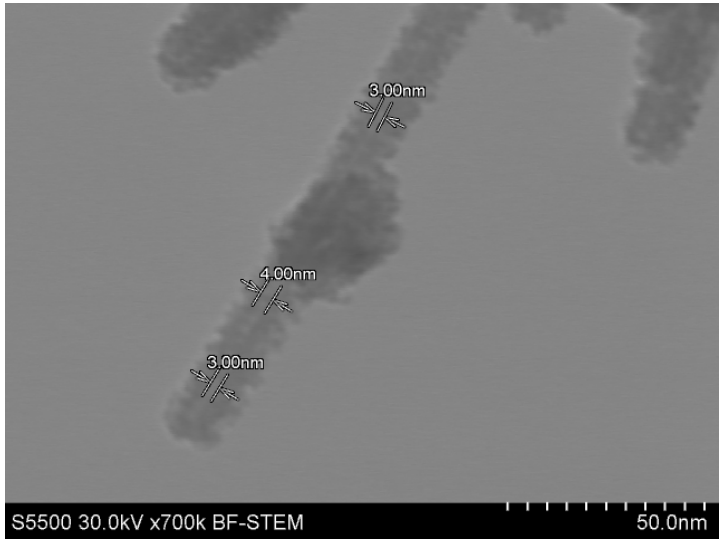
Optimizing CNT-CNT Contact: In polyethylene

- *March – May 2009*
- SWNT (Southwest CG 100): 10wt% loading
- MDPE
- Small scale tests – samples not extruded
- Good dispersion
- $1*10^{-2}$ Ω•cm to $1*10^{0}$ Ω•cm with
  - melting/heating
  - electrical current conditioning



Optimizing CNT-CNT Contact: novel doping

- *Fall 2009*
- Patent in process
- Background
  - Reversible charge-transfer doping which encourages metallic states for bulk SWNT – much existing research
  - Electrochemical and direct vapor/ liquid methods
- Novel solution:
  - Fabrication – new combination of materials
  - Initial research shows conductivity of raw SWNT increased
  - Hoped for higher conductivity with further refinement



Optimizing CNT-CNT Contact: metal additives

- *Sept - Nov*
- Simpler than chemical doping or coating
  - Cheaper processing, suitable for **bulk** fabrication
  - Increase conductive pathways
  - Composites so far:
    - SWNT + nanoscale Al + MDPE
    - SWNT + nanoscale Ag + MDPE
    - SWNT + other additives + MDPE

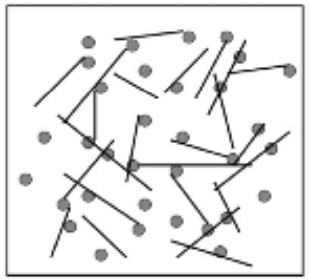
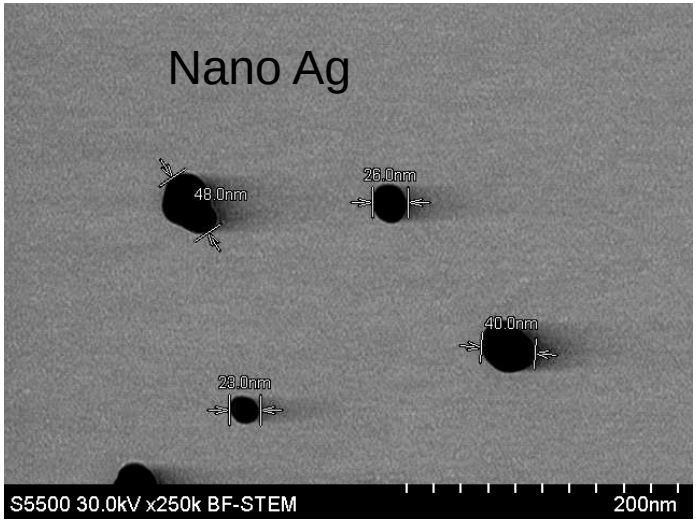
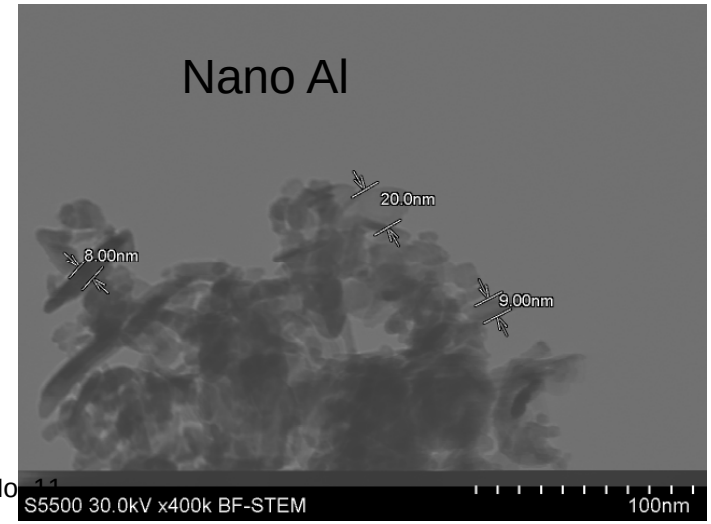


Diagram: Liang et al, ADV ENG MAT 2007, 9, No. 11





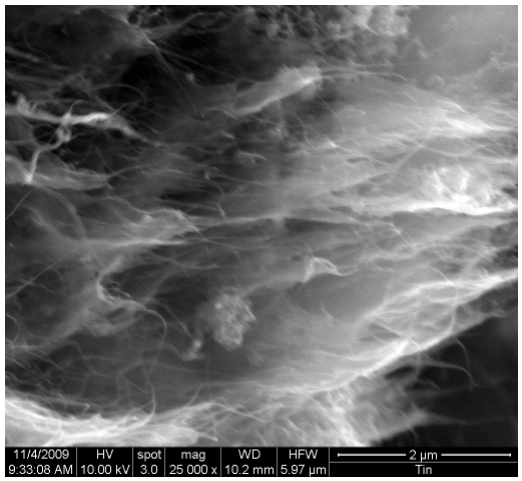
Optimizing CNT-CNT Contact: Novel processing route

- *Fall 2009*
- Patent in process
- Previous work:
  - SWNT with microwaves: Dr. J.M. Tour et al, Rice University
  - Curing of composite using SWNT and microwaves
    - Higginbotham, Moloney, Tour et al Composites Science and Technology 68 (2008) 3087–3092
- Rapid and efficient transfer of energy from microwave to thermal

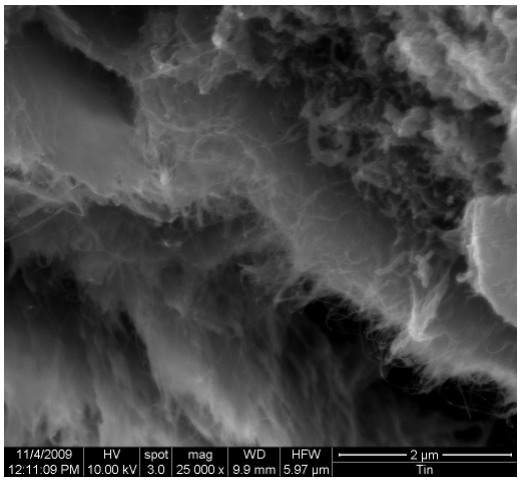
Optimizing CNT-CNT Contact: high wt% CNT loading

- *September-November 2009*
  - Winey dispersion procedure
  - Increase probability CNT-CNT contact
- 50wt% CG 100 in MDPE
  - $1.4 * 10^{-1}$ Ω•cm
- 70wt% CG 100 in MDPE
  - $6*10^{-2}$ Ω•cm
- 90wt% CG 100 in MDPE
  - $3*10^{-2}$ Ω•cm
- Similar bulk attributes across the samples
  - Higher wt% possible, but necessary?

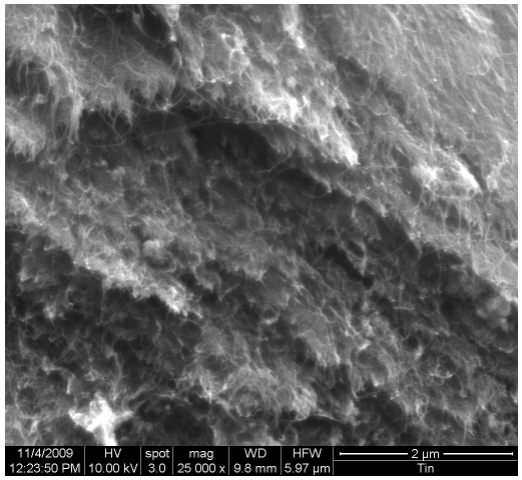
Optimizing CNT-CNT Contact: high wt% CNT loading



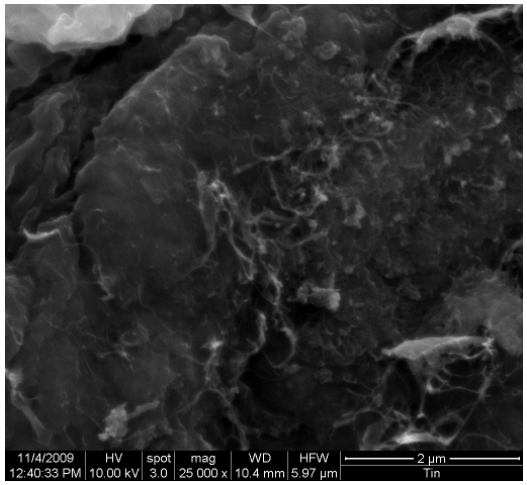
30wt%



50wt%



70wt%



90wt%

CNT-CNT Optimization

- Produced PNU with SWNT wt% up to 90wt%
  - $3*10^{-2}$ Ω•cm – no optimization
- Optimization of CNT-CNT connection reduced resistivity
- Preferred CNT type: m-SWNT
- Novel processing and doping techniques reduced raw SWNT resistance by 10-90%
- Future work:
  - Nanoscale measurement
  - Novel processing technique – refinement
  - Novel doping – refinement
  - Combine processes

nanoUmbilical Workshop

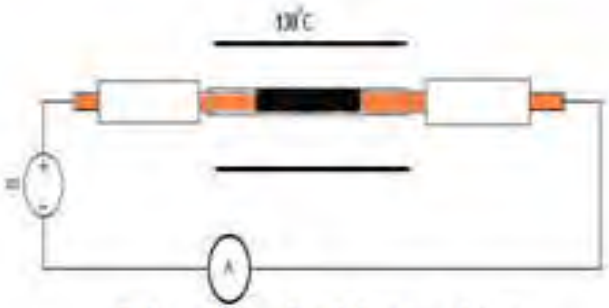
Steps to Achieving Conduction

D.Chakravarthi, A.Salman, P.Moloney, Y.Zhao, L.Jacob, M.Searfass, D.Hulsey, E.V.Barrera

Outline

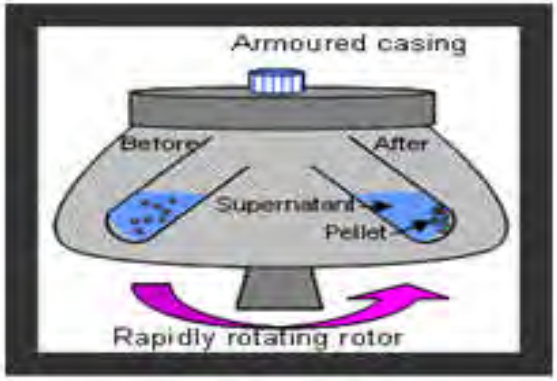
- Dispersion of carbon nanotubes (CNTs).
- Decanting the CNTs – solvent suspensions.
- Processing CNTs – medium density polyethylene composites (MDPE).
- Electric field studies on CNT – MDPE composites.
- Outcomes.

Process



Electric field studies

Dispersion of CG-SWNTs in dichlorbenzene



Decanting process

Composite Processing

NanoRidge RICE UNIVERSITY Technip DUCO Chevron

Dispersion of Carbon Nanotubes

- Carbon nanotubes tend to agglomerate due to the strong Van der Waal's attraction .
- In order to effectively use their properties, good dispersion of CNTs in the solvent / polymer is very essential.
- Good dispersions can be achieved by using suitable solvents and surfactants, sonication, homogenizing etc.

Macroscopic Dispersion behavior in solvents

Precipitation /unstable

Separates into two phases : a precipitant and a clear liquid

Stable / No precipitation

A homogeneous black stable suspension with no visual precipitation

- Common solvents used to disperse CNTs are N-methylpyrrolidone, dimethylformamide, tetrahydrofuran and dichlorobenzene.

- In our studies we used dichlorobenzene to disperse the CNTs and the concentration was maintained at 0.2 mg / ml.

- The CNT – dichlorobenzene suspensions were sonicated for 3 hours using a probe sonicator.

Use of a good solvent and sonication aided in stable dispersions of CNTs

Decanting Studies

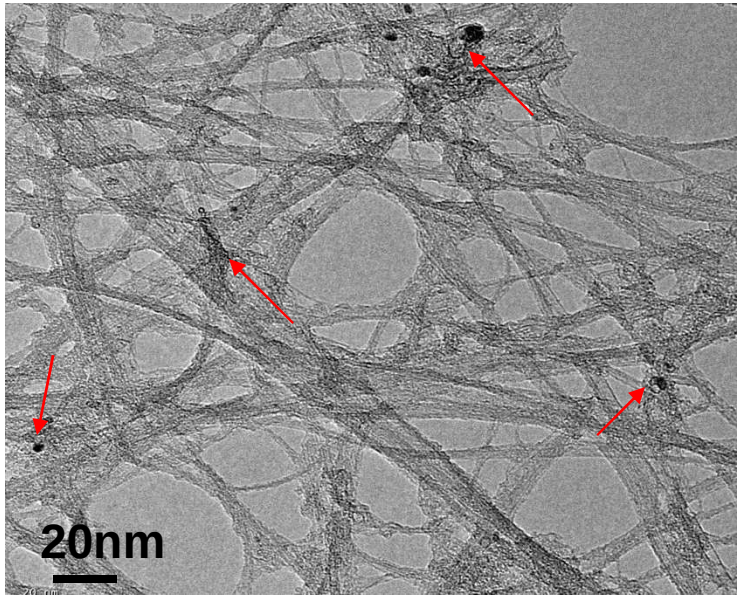
- Centrifuging the CNTs removes the heavier catalyst particles, large agglomerates and amorphous carbon from the nanotube suspensions leaving behind non-agglomerated, well dispersed CNTs.

- CNT / dichlorobenzene suspensions were divided into 50 ml aliquots for decanting studies.

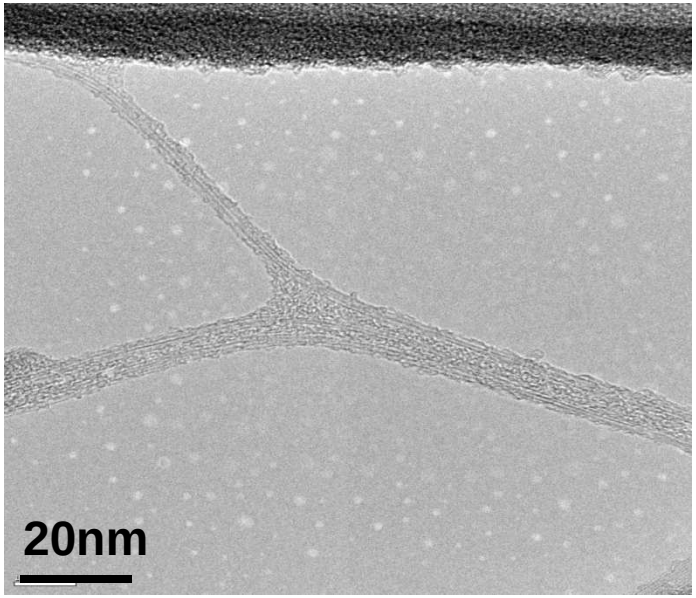
- Samples were centrifuged at various g's (15000, 50000, 85000) for different time intervals (15 , 30 and 45 minutes).

- Our studies revealed that the heavier particles fall out of the suspension only at the highest g force when centrifuged for 45 minutes.

Characterization of decants



Before Decanting



After Decanting (85000 g for 15 minutes)

- A weight analysis on the pellet showed that 30% of the original sample sedimented out of the solution.
- Clean non-agglomerated CNTs and smaller diameter bundles of CNTs were obtained.

- De-agglomeration is the synergy between decanting and dispersion of CNTs.
- In our studies we successfully dispersed the CNTs in dichlorobenzene
- Decanting process removed the amorphous carbon, heavy catalyst particles and, heavy agglomerates leaving behind clean, smaller diameter bundles and single CNTs.

Deagglomerated CNTs can be used in processing of polymer composites because their excellent electrical , mechanical and thermal properties can be efficiently utilized.

Composite Processing (Winey Method)

Sonicated 10 wt% CG SWNTs
or HiPco SWNTs
(0.2 mg/ml)
in dichlorobenzene (DCB) for 3 hours

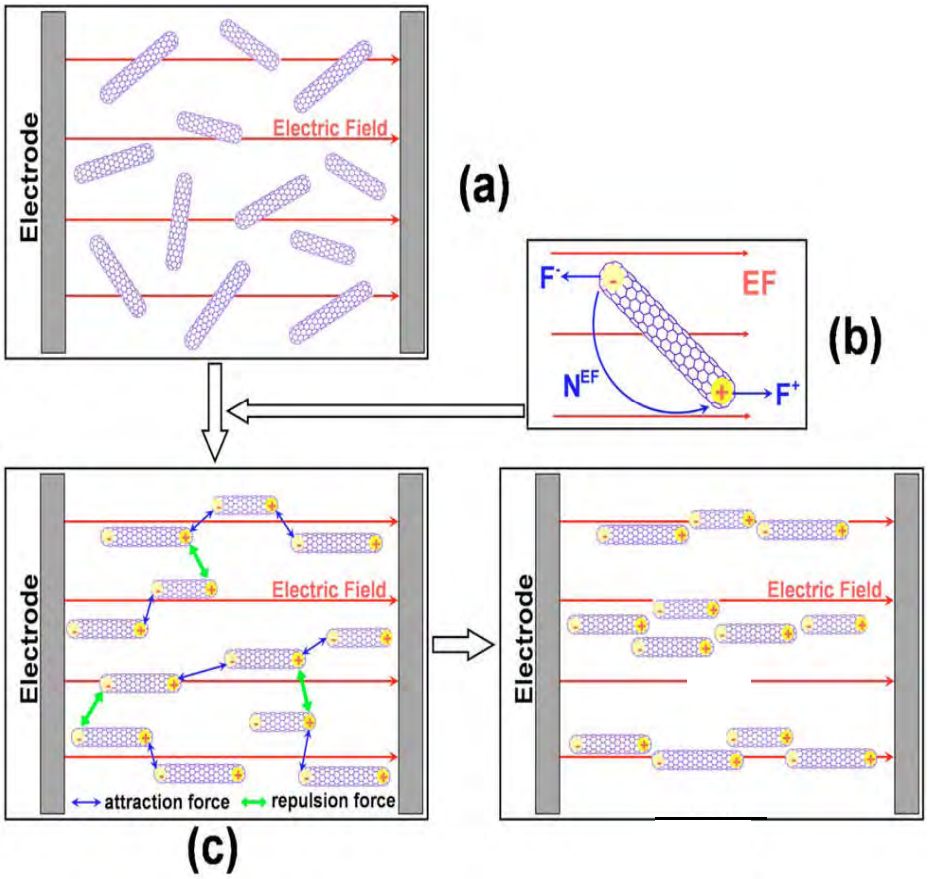
Heated the above
dispersion to 110 °C and
added MDPE
dissolved in DCB at 110 °C .

CG-SWNTs or Hipco SWNTs in
DCB were then cooled to below
70 °C while simultaneously
Sonicating the mixture.

Further the composite was vacuum
Filtered to remove the DCB and dried at
100 °C

Haggenmueller.R *et al* , *Macromolecules 40,* 2417-2421,2007.

Alignment of Carbon Nanotubes in a medium under the effect of electric field



a. Polarization of SWNTs.

b. The electric field induces a dipole moment on the nanotubes.

c. Rotational forces makes them align in the direction of the field.

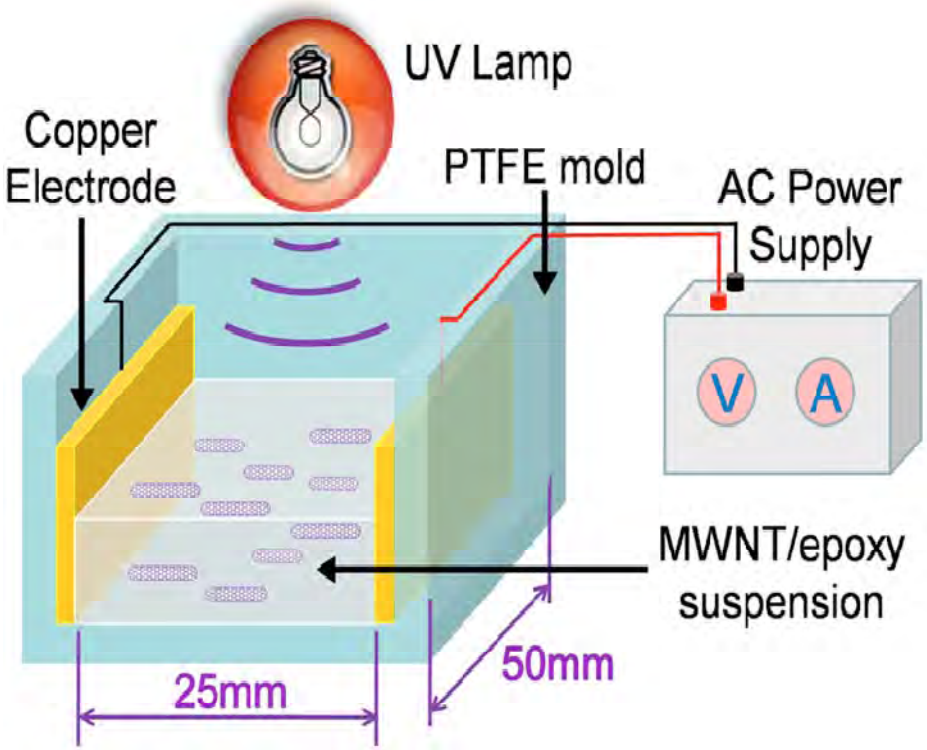
Zhu *et al*, Journal of Applied Physics, **105**, 054319 (2009).

Illustration of CNT alignment in an electric field

- Functionalized CNTs suspended in THF were used.
- At low DC field (<100 V) the nanotubes moved from the suspension towards the electrode and deposited on the electrode.
- At high DC field (>100V) the nanotube bundles begin to align perpendicular to the electrode surface.

Kamat.P.V *et al*, J. Am. Chem. Soc. **126**, 10757 2004.

Alignment of CNTs in polymer composites



Zhu *et al*, Journal of Applied Physics, **105**, 054319 (2009).

- MWNTs nanotubes in epoxy suspension were used.
- AC voltage of 2000 V and 2000 Hz peak to peak was applied for 10 minutes to study the alignment.
- UV light was used to irradiate the samples to polymerize the suspension.
- The resistivity of the composite reduced from 10^{15} ohm.cm to 10^{10} ohm.cm by addition of 0.5 wt% MWNTs

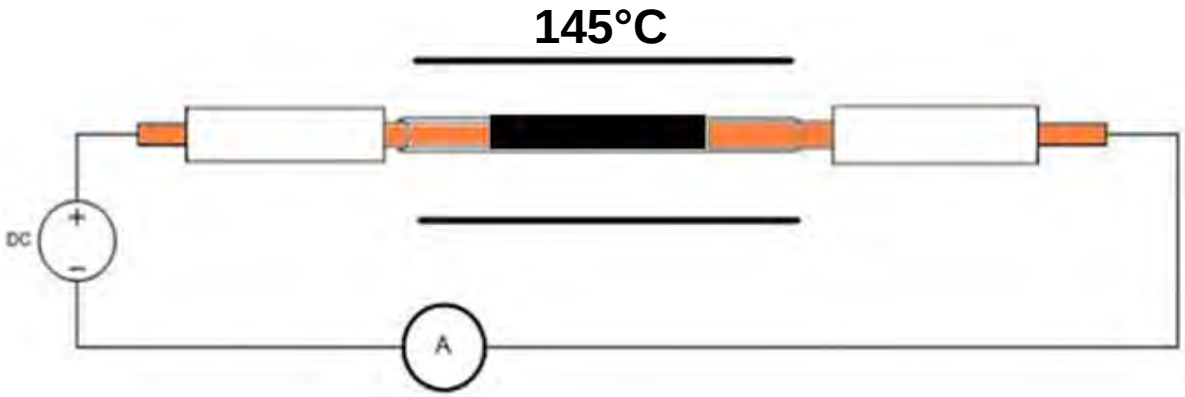
Effect of DC electric field on medium density polyethylene / CG-SWNT composites

- Using the previously discussed studies, we incorporated the principles of CNT alignment under the effect of electric field within our CNT / MDPE composites.

- 10 wt% CG-SWNTs, 10 wt% Purified HiPco SWNTs in MDPE were used.

- AWG 8 multistranded copper wire (18 strands) and silver soldered single core wires were used in our study.

Process



- Samples were heated to 145 °C for 30 minutes before the electric field was applied.
- Before applying the electric field, the distance between the copper leads was maintained at 1.5 cm.
- Low DC electric field was applied and the voltage was increased from 1 to 8 volts.
- Samples had to be conditioned a minimum of three times to be able to carry high currents.

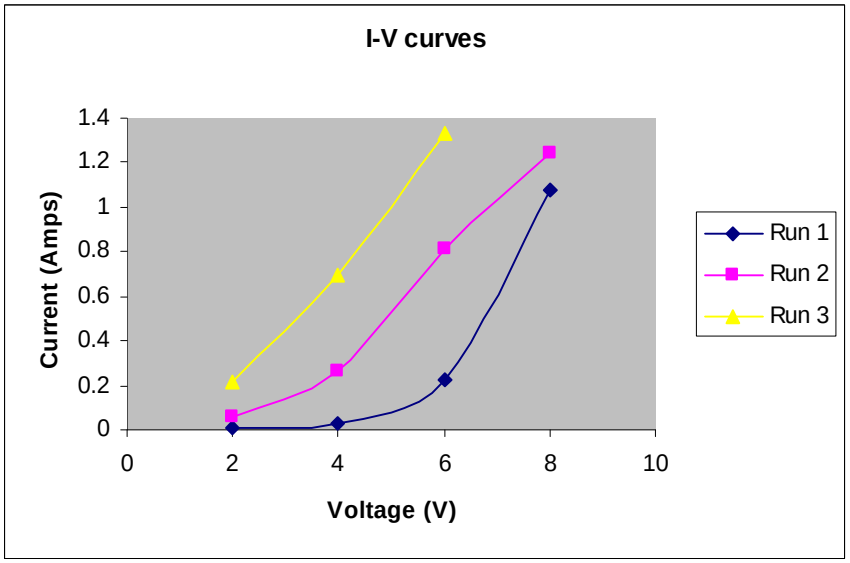
Challenges and Solutions towards Optimizing the Process

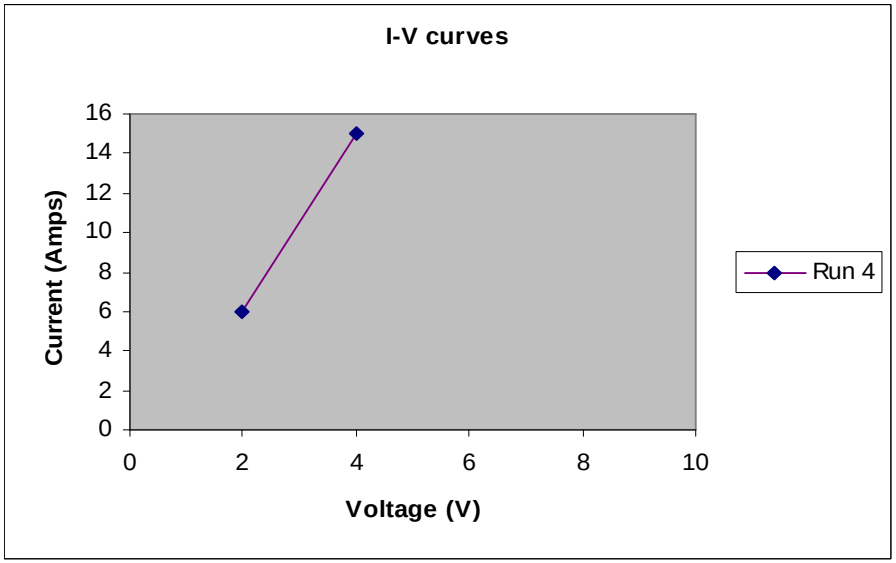
	Challenge	Solution
1	For CNTs to effectively align in the polymer, the polymer has to have low viscosity. **Resistivity (~ 200 ohm.cm)**	Our composites were heated to 145 °C to allow the nanotubes to align and form a network. **Resistivity (~ 2.5 ohm.cm)**
2	For the electric field to be effective, there should be a solid contact between the copper leads and the sample. **Resistivity (~ 2000 ohm.cm)**	The sample was compacted between the leads by applying pressure and the leads were clamped in place. **Resistivity (~ 60 – 100 ohm.cm)**
3	Unlike all previous studies where the polymers are either photo curable and UV curable, PE is not UV curable or photo curable **Resistivity (~ 50 – 100 ohm.cm)**	A low voltage electric field was applied when polymer was allowed to harden after alignment tests **Resistivity (~ 0.5 ohm.cm – 10 ohm.cm)**

	Challenge	Solution
4	Void formation which will prevent a continuous network for electron flow. **Resistivity at 145°C (~ 2.5 – 5 ohm.cm)**	Samples were conditioned and after each conditioning run the leads were pushed in further to eliminate the voids. **Resistivity at 145°C (~ 0.02 – 0.09 ohm.cm)**
5	Upon applying force on the copper leads, the polymer flows on the exterior of the leads due to a minor difference between the inner diameter of quartz tube and the copper leads. This decreases the amount of polymer between the leads.	Sealing the area between the copper lead and inner diameter of the quartz with Teflon and holding the copper in place using a insulating tape and clamp reduced the polymer flow.

A unique process of electrically conditioning the MDPE / CNT composites was developed.

Example of current – voltage characteristics for MDPE / 10 wt % purified HiPco samples





- After each run, the composite was able to carry higher currents at the same voltage indicating a decreasing in the resistivity of the composite.
- The **sample was able to carry 16 amps of current** at 145 °C because of a very good network formation of CNTs.

Electrical Resistivity of MDPE / Carbon nanotube composites

Sample AWG 8 – 18 strand copper wire as leads	Resistivity (ohm.cm)	Diameter (cm)	Surface area (cm^2)
Polyethylene (MDPE)	10^{15}	0.394	0.12
10 wt% CG / MDPE	~ $1* 10^3$ – $1.5* 10^3$	0.394	0.12
10 wt% CG / MDPE (application of electric field) at high temperatures)	~ $4*10^{-2}$ – $6*10^{-2}$	0.394	0.12
10 wt% purified HiPco / MDPE (application of electric field at high temperature)	~ $2*10^{-2}$ – $6*10^{-2}$	0.394	0.12
10 wt% CG / MDPE (application of electric field at room temperature)	~ $5 * 10^{-1}$ – 10	0.394	0.12
10 wt% purified HiPco / MDPE (application of electric field at room temperature)	~ $2 * 10^{-1}$ – 5	0.394	0.12

Sample	Resistivity (ohm.cm)	Diameter (cm)	Surface area (cm^2)
10 wt% purified Hipco / MDPE (application of electric field at high temperature) (Single core copper lead)	~ $7 * 10^{-2} – 9* 10^{-2}$	0.394	0.12
10 wt% purified Hipco / MDPE (application of electric field at high temperature)	~ $4.5 * 10^{-1} - 8 * 10^{-1}$	0.2	0.031

- To ensure repeatability of the process 10 to 15 samples were tested in each category described in the table.
- Initially it required 5 to 6 runs for the sample carry high currents at low voltages, but with process optimization the number of runs reduced to 4.
- With use of single core wire , it required 3 to 4 runs to condition the sample and the time required for conditioning was reduced by 30 minutes.

- Composites with 10 wt % CNT (CG – SWNTs / HiPco) showed the best resistivity at elevated temperatures.

- After the application of electric field : five order decrease in the resistivity at elevated temperatures and four decrease at room temperature was obtained for CNT / MDPE composites.

- The optimal distance between the leads was found to be 0.7 to 0.8 cm for the best conducting samples.

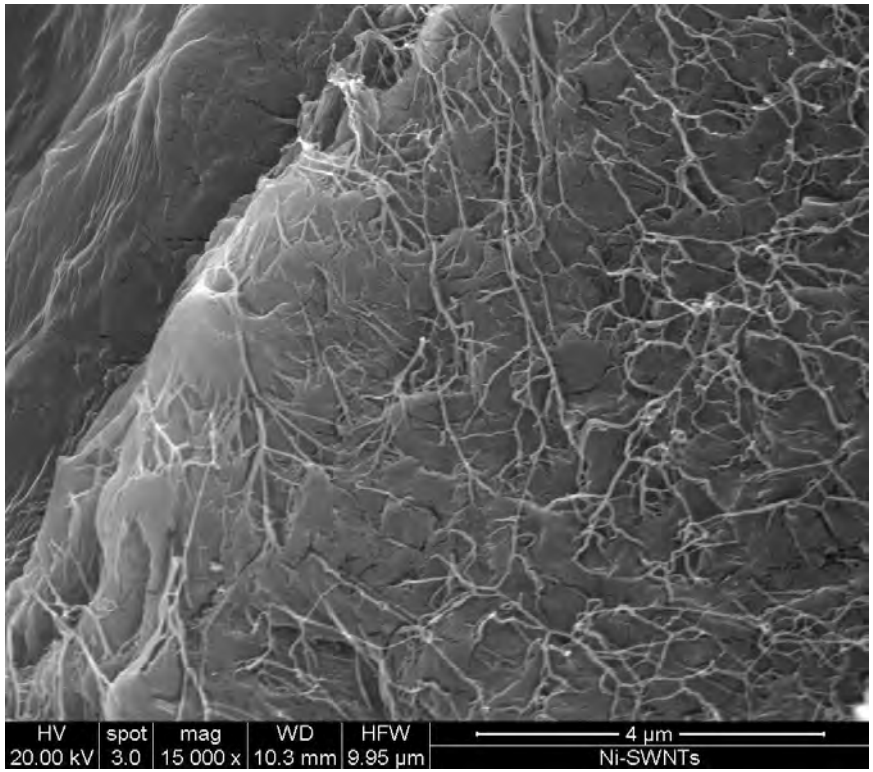
- A reduction in resistivity can be due to two reasons :
  - At high temperatures, when the polymer melts, the nanotubes tend to align to form a network because they are free to rotate under the influence of electric field.

  - Also, in areas which are polymer rich, resistive heating of the polymer due to high current would bridge the gap between nanotubes and this in turn will lead to a continuous network formation.

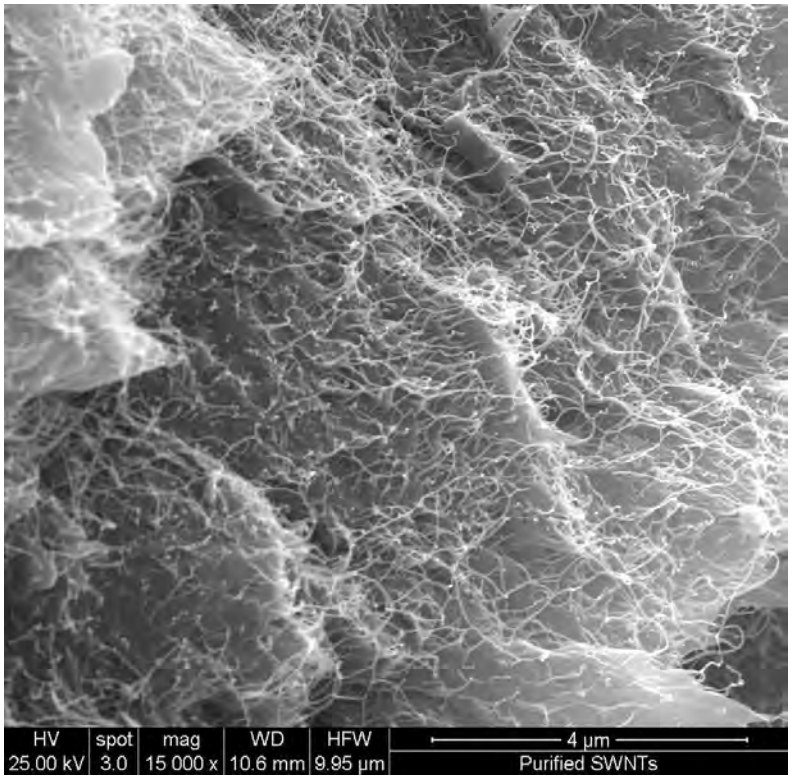
De-agglomeration , continuous network formation and alignment, proper contact, reduction in void formation are some of the important factors that reduced the resistivity of the composite.

NanoRidge RICE UNIVERSITY Technip DUCO Chevron

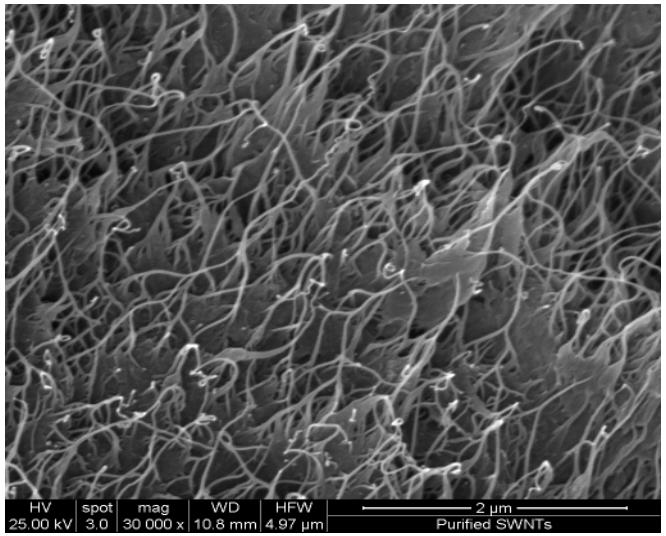
Characterization of MDPE / SWNT composites

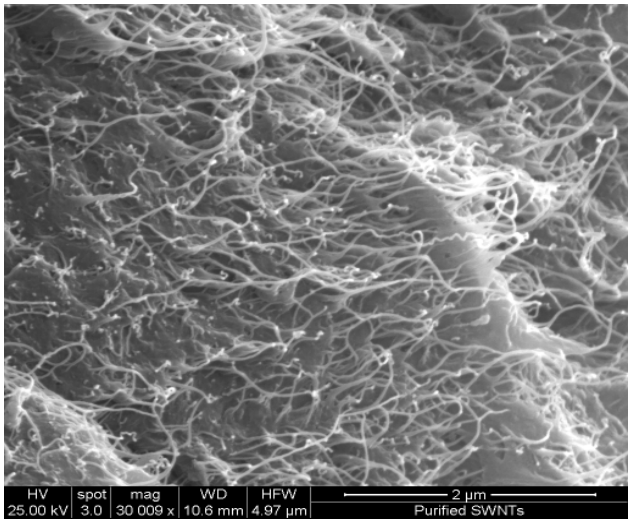


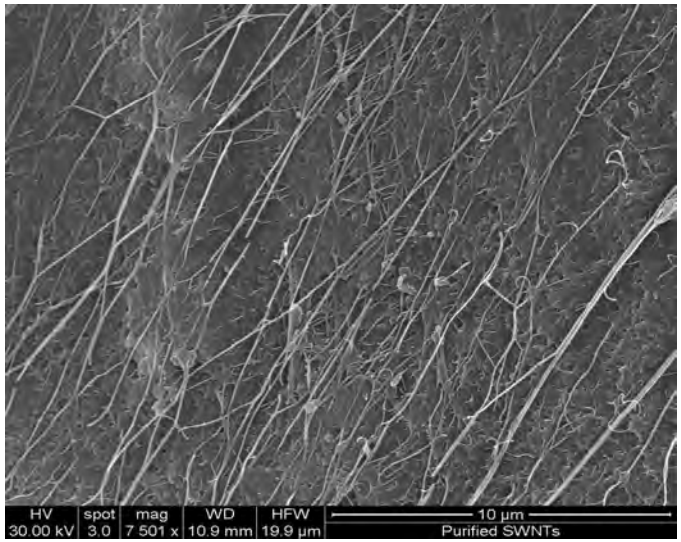
Before Electric Field



After Electric Field







Due to electric field:

a) In some areas, alignment of CNTs was observed.

b) In most areas, a net alignment and a better network of CNTs was observed.

Outcomes

- Efficient dispersion and decanting of CNTs.
- A unique process to condition the MDPE / CNT composites was developed.
- Continuous network formation by bridging gaps under the influence of electric field, aided in improving the conduction in MDPE / CNT composites.

Resistivity of the composite decreased by 17 orders of magnitude as compared to neat medium density polyethylene composite.

nanoUmbilical
Workshop

Steps to Manufacture the PNU

Yao Zhao, Divya Kannan Chakravarth, Padraig Moloney,
Lori Jacob, Dean Hulsey and Dr. Enrique V. Barrera

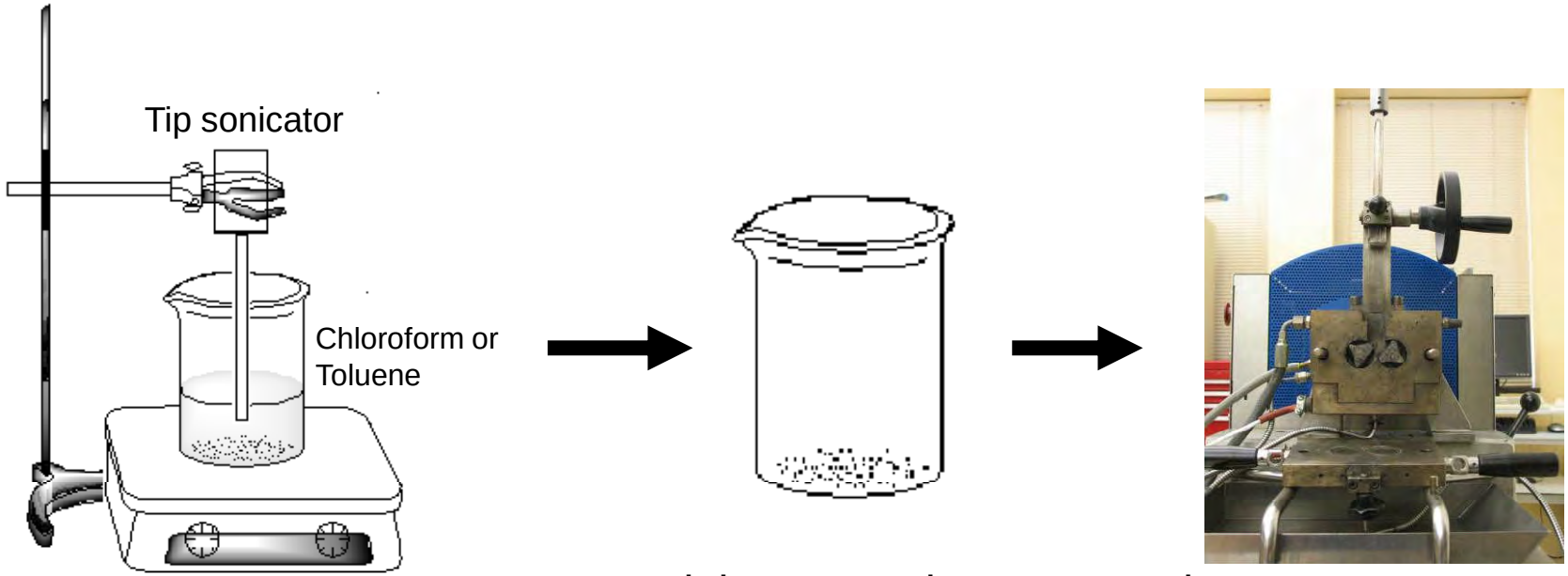
Outline

- Dispersing nanotubes in the polymer matrix
- Manufacturing fibers and wires
- In-situ and post treatments

Dispersing nanotubes in the polymer matrix

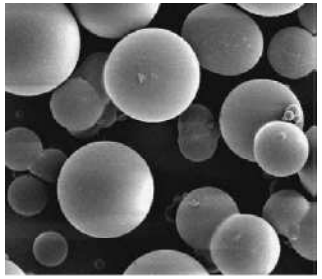
- Nanotubes/HDPE (RU developed process)
  - Incipient wetting
  - Mechanical mixing
- Nanotubes/MDPE (Use of autoclave)
  - Creating porous MDPE powder
  - Solution mixing assisted by ultrasonic agitation
  - Mechanical mixing

Dispersing CNTs in the HDPE matrix



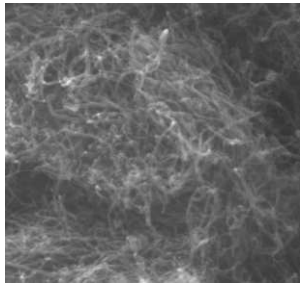
Incipient wetted HDPE powder

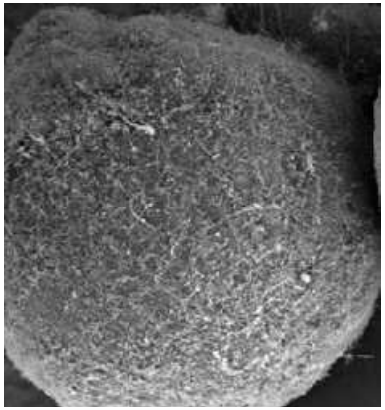
HDPE powder



+

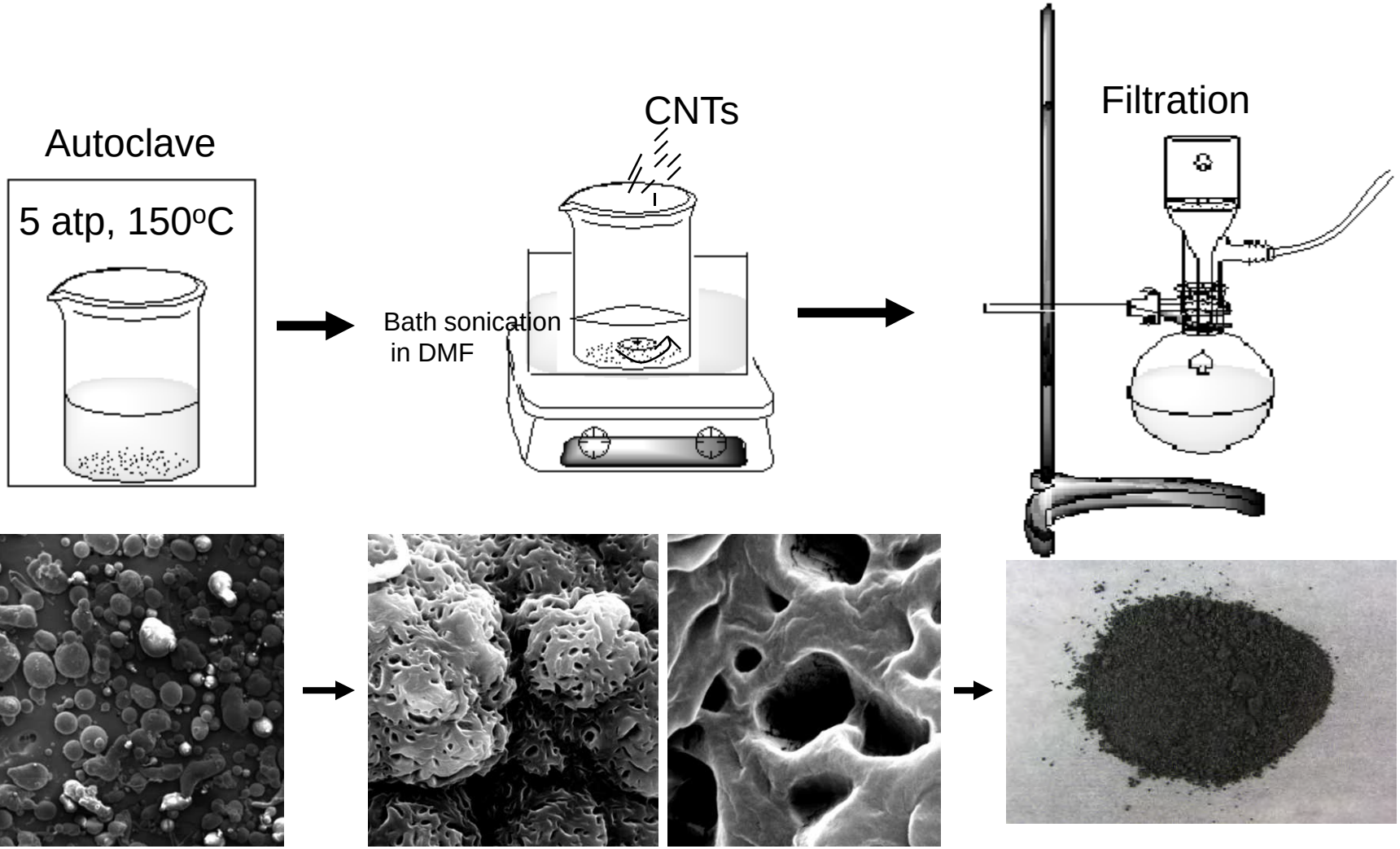
CNTs





Masterbatch of the composite

Dispersing CNTs in the MDPE matrix



Manufacturing fibers

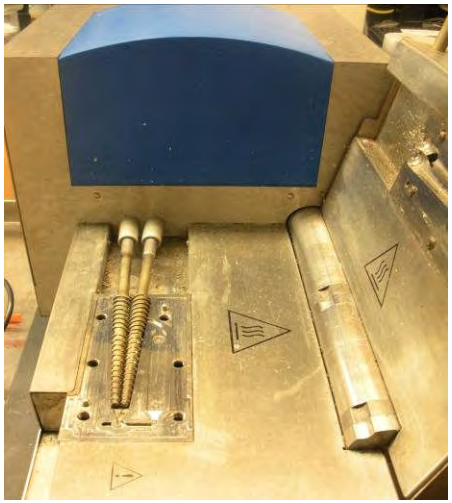
- Solution spinning
  - Relatively slow
  - Removing solvent is required
- Electrospinning
  - Fiber size is small (nano-micro size in diameter)
- Melt spinning
  - High production
  - Produced fibers suitable for macro applications

Melt spinning

1) Injection Molding
3 g size

3) Haake Extruder
100 g size

2) Haake Mini lab
10 g size

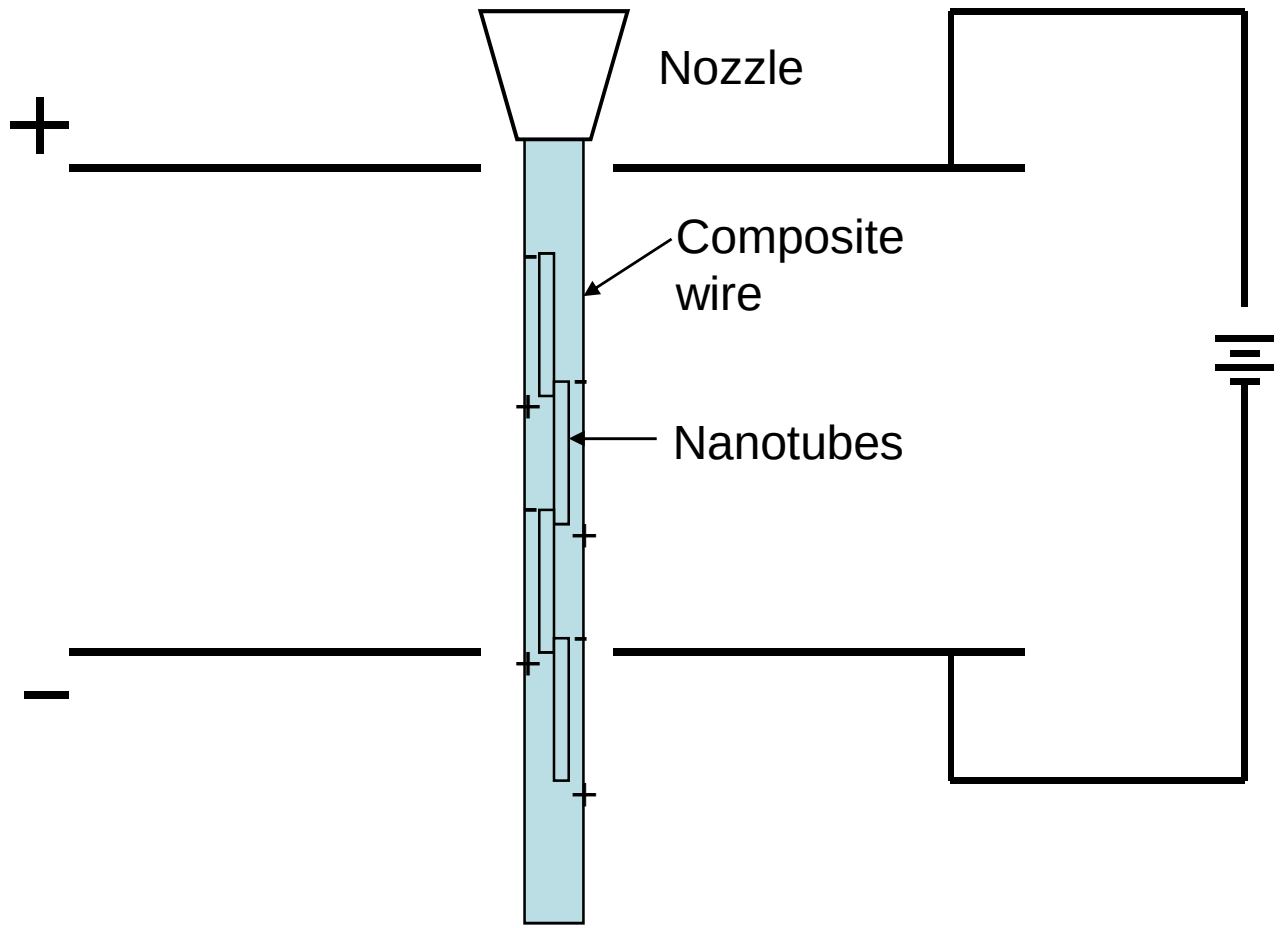


4) M-scientific Extruder
200 g size

In-situ and post treatments

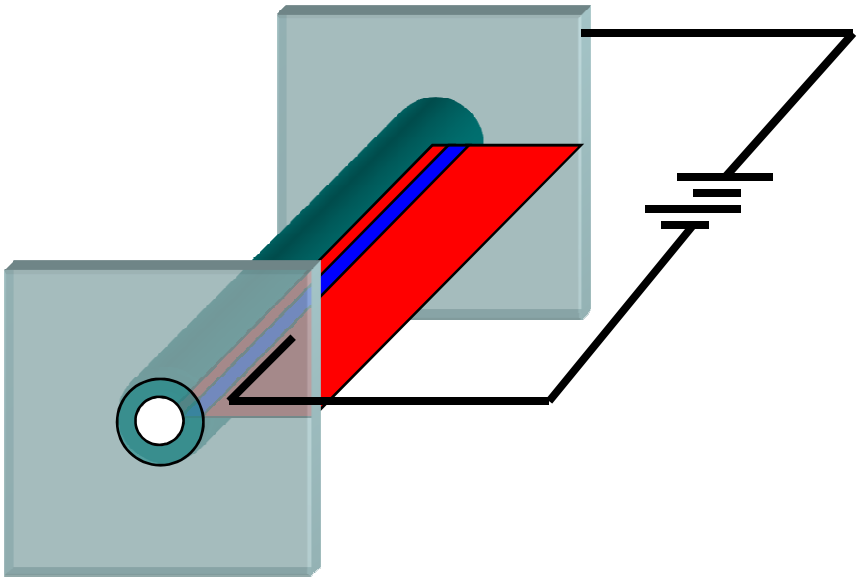
- In-situ electrical field assists alignment
- Post treatments
  - Annealing
  - Doping
  - Passing current
  - Hydrostatic pressure

2 functions of the electrical field

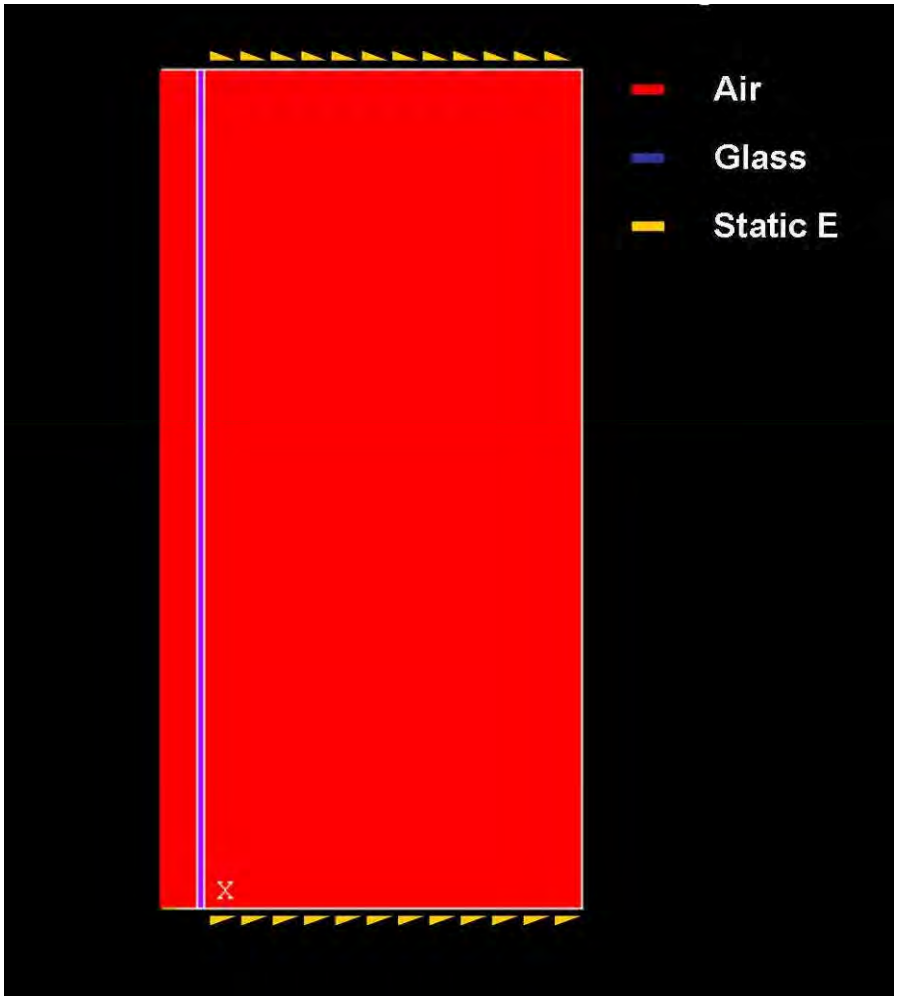


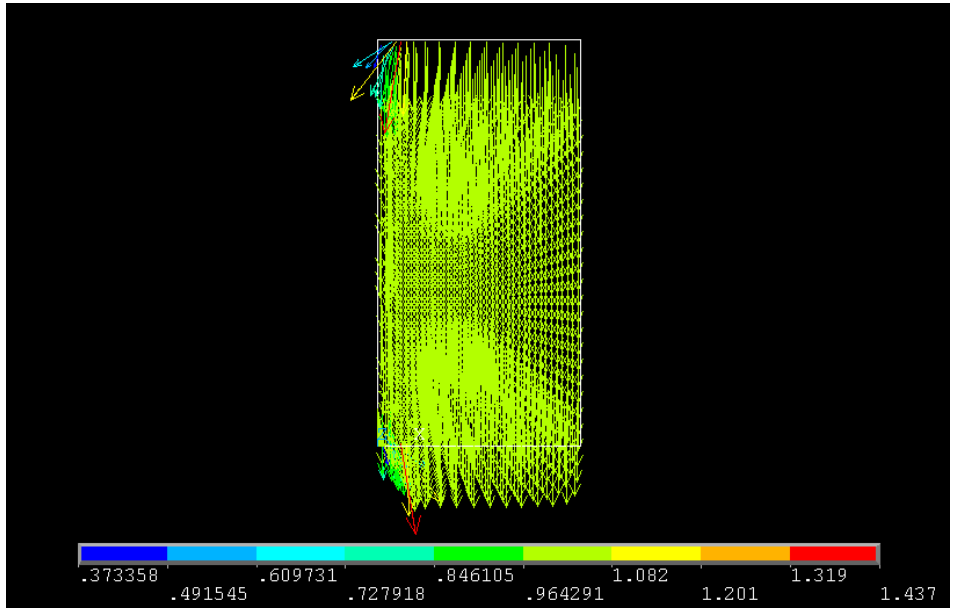
- NTs are dipolarized by the external electrical field.
- The opposite charges bring NTs closer and enhance alignment.

Electrical field setup design

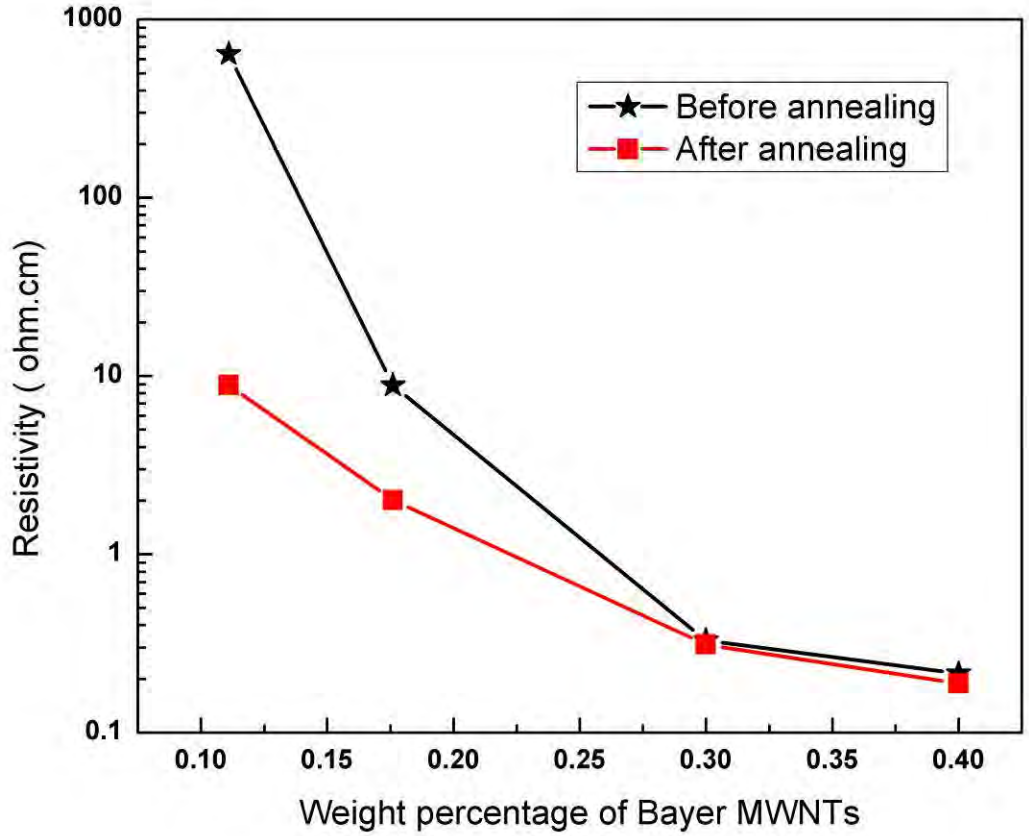


Finite element analysis



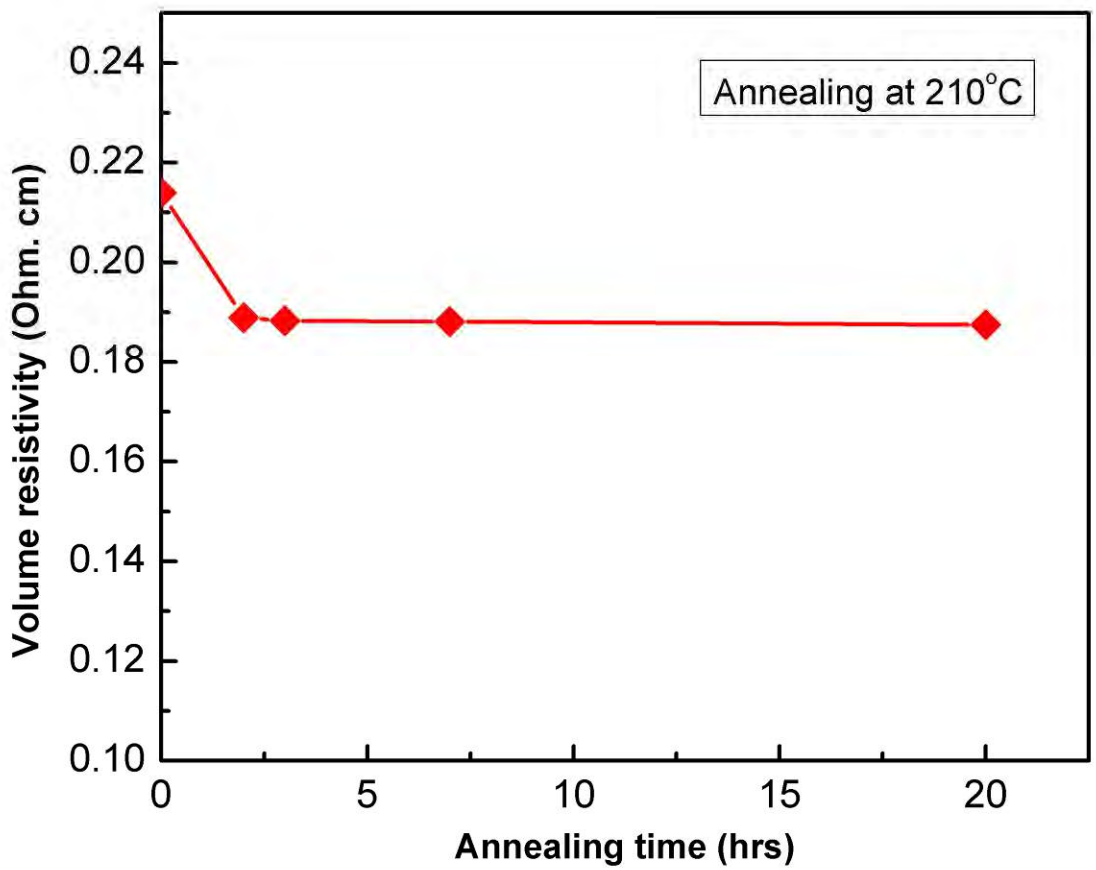


Annealed vs. unannealed



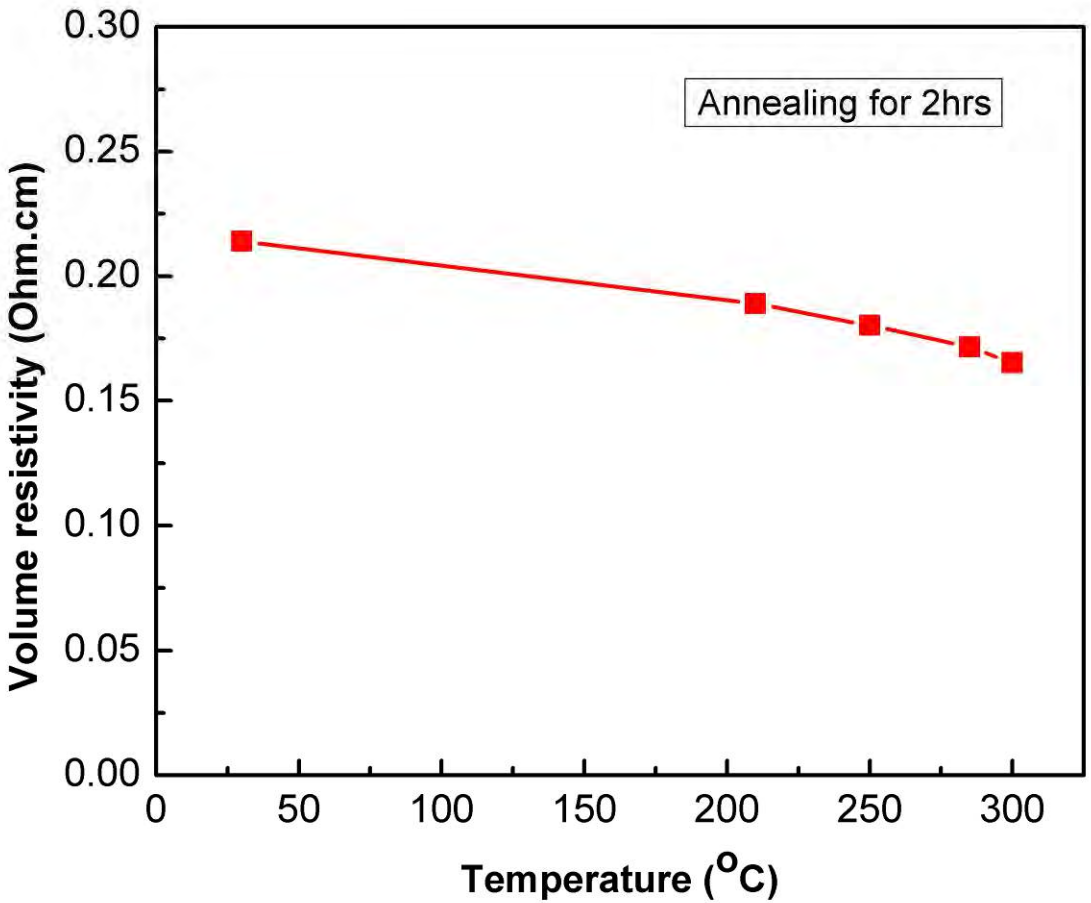
The annealing effect on improving the conductivity is more pronounced in the Low loading ratio region. The effect dims when the loading ratio reaches 30 wt% and Beyond.

Annealing time effect



Annealing time longer than 2 hrs does not help in improving the conductivity.

Annealing temperature effect



As annealing temperature increases, the conductivity of composite wires increases slightly.

Iodine doping

Sublimation temperature of iodine is 113.7 ^{o}C
The doping was taken place at 130 ^{o}C for 8 hrs.

The resistivity has been reduced by a factor of 3.
Original: $4.17*10^{-1}$ ohm.cm.
After doping: $1.41*10^{-1}$ ohm.cm.

Other than Iodine doping, $SOCl_2$ and Li doping
Have been studied.

Steps to Manufacture the PNU

HDPE Pellets

Grinding

HDPE Powder

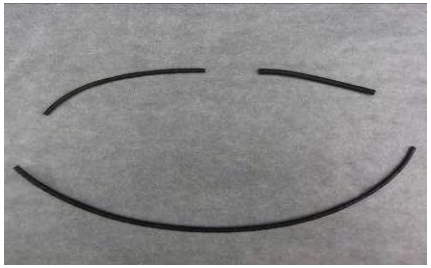
Incipient wetting

Mixing

Hot pressing

Cutting

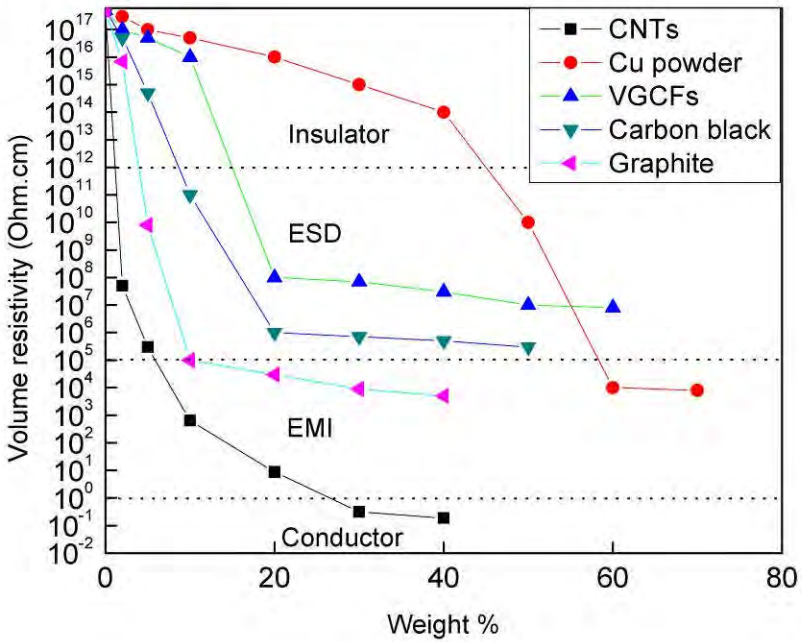
Extrusion



Schematics of Processing Procedures

Conclusion

- Progress achieved

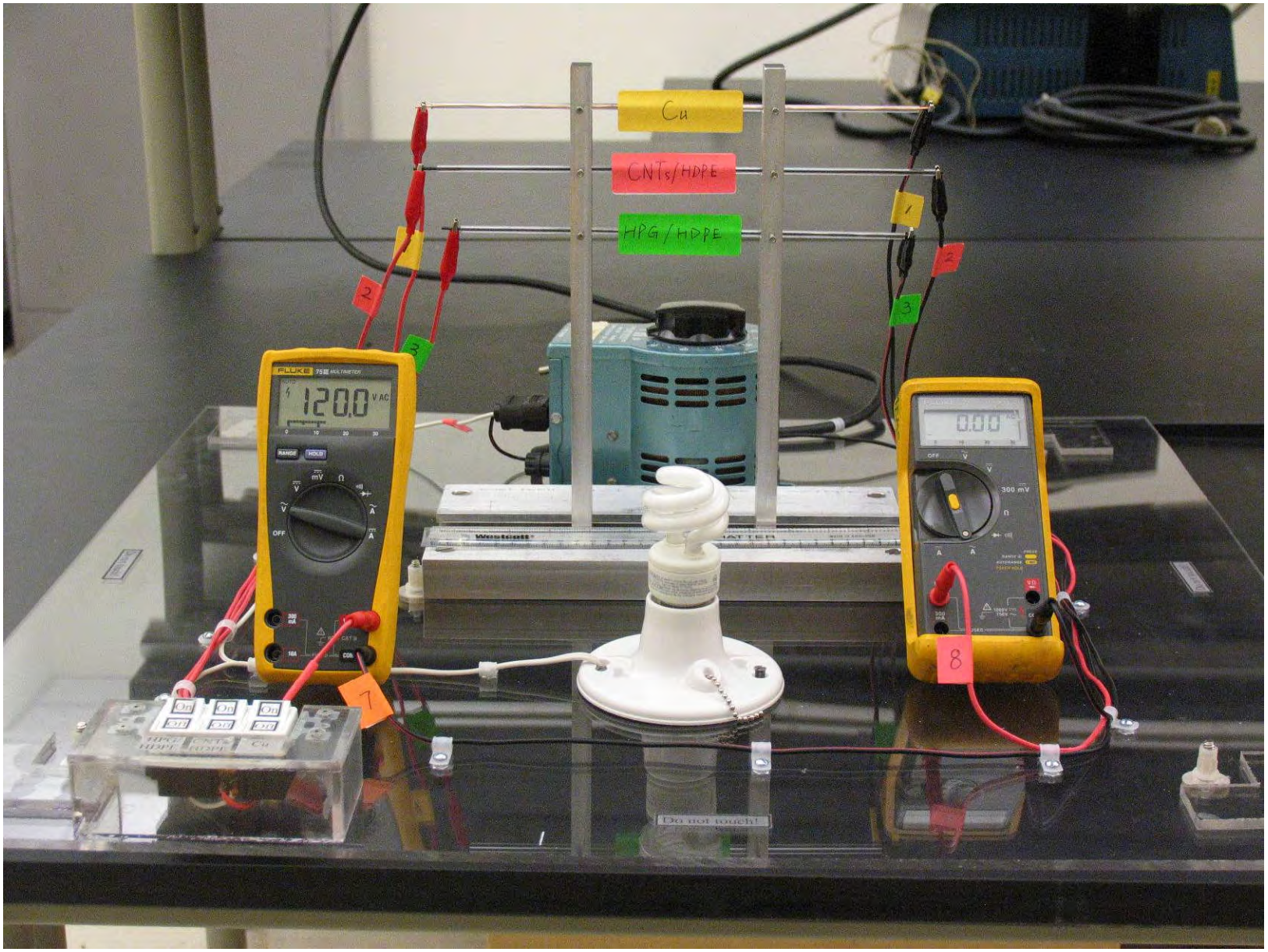


- Semi-continuous conductive composite wires have been successfully fabricated.

Outcome

- Key processing steps have been identified.
- Scale up the quantity of materials processed by melt spinning.
- Device for the electrical field use has been produced.
- Annealing is an effective post-processing step for low loading samples.
- Doping reduces the resistivity.

Demonstration setup



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Workshop

Outcomes

Enrique V. Barrera

Department of Mechanical Engineering and Materials Science, Rice University, Houston, TX 77005

Outline

- Goals
- Approach
- Completed Tasks
- Processing Approach
- Samples Produced
- Concerns and Issues
- Proven Approach
- Outcomes
- Demonstrations
- Closing Comments

Program Goals: Deliverables

(1) Bridge the gap between engineering science and manufacturing technology to produce a piece of wire.

The wire conductor will be a polymer-Nanotube composite that is half the diameter of a Cu conductor that can carry 500 amps at the same voltage used for the Cu conductor.

We will also produce the following:

(2) Report to RPSEA suitable for public release.

(3) A workshop to feature advances in power conductors for oil and gas use.

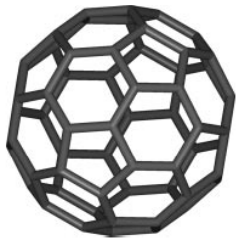
Nanotubes: Data Sheet Engineer's Perspective: Broad Property Range

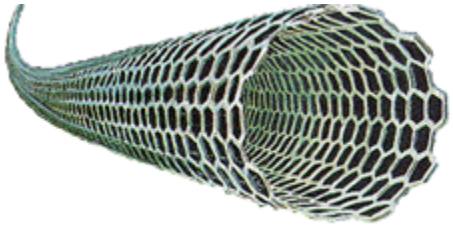
Fullerenes (C_{60})

- **Low thermal conductivity** (0.4 W/m•K)
- **Point scatterer** (~ 1 nm spherical particle)
- **Grain boundary and interfacial effects**

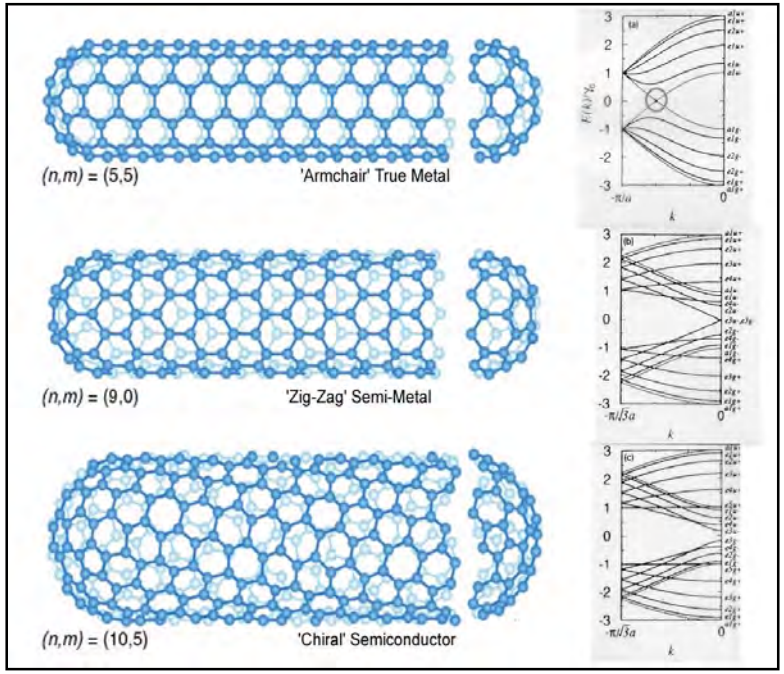
Single Walled Carbon Nanotubes

- Dimensions: 1nm (dia.), 0.3 – 100 μm (length)
- Density: 0.89g/cm^3
- Tensile strength ~50GPa
- Tensile Modulus ~1TPa
- Elongation to failure ~5%
- Electrical Conductivity ~1800-2000 ohms^{-1}
  Semiconducting to conducting like copper
- Thermal conductivity (C_{60}) low in
  transverse direction and high (diamond)
  along tube axis (~2500 W/m•K)
- Nanoscale scattering defects
  - Tubes intact or removed in situ (nanovoids)
- Bonding by van der Waals or by functionalization





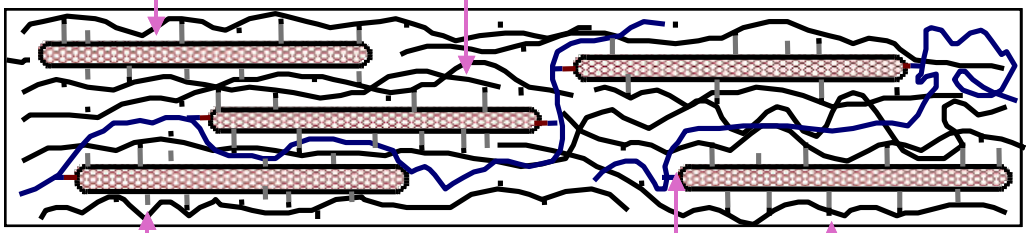
Background: Nanotechnology Basis for the PNU



Fully Integrated Nanotube Composites to Achieve Cold Forming

Align single nanotubes by shear/elongational processing.

Remove excess and unwanted matrix.



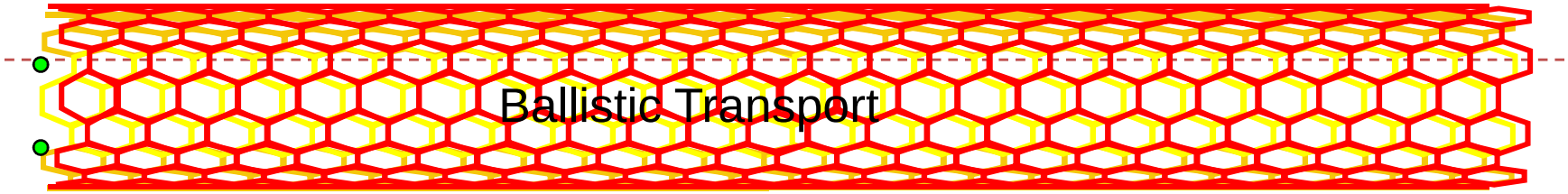
Functionalize (i.e., polymerize) to fully integrate.

Identify appropriate functionalization: Side wall vs. end attachment.

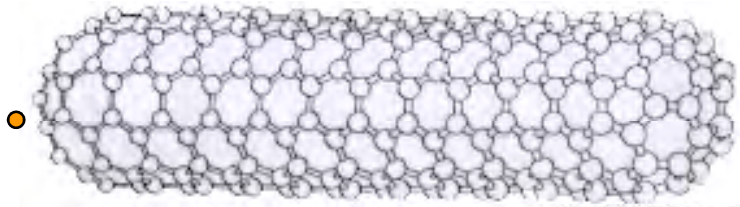
Of the dozens of known nanotube types, one third are metallic; the rest are direct band-gap semiconductors. The metals, especially the 'armchair' tubes, have been shown to conduct electricity at least as well as copper, and perhaps some ten times better.

A PNU consist of aligned SWNTs in a polymer matrix such that misalignment assures electrical contact while providing for robust mechanical strength. Use of metallic SWNTs ensures high electrical conduction. Optimizing the concentration of the SWNTs ensures costs control and near term use.

Background: Electron Transport Mechanisms

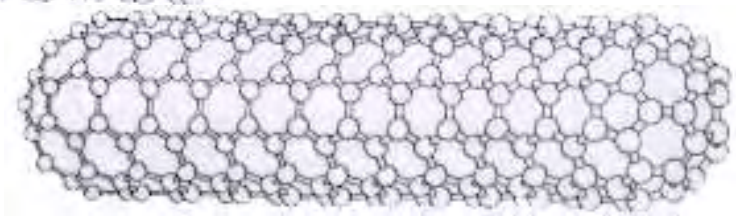


Ballistic conduction allows electrons to flow through the material without collisions. The collisions cause the electrons to slow down, and cause the material to heat, effectively creating resistance in the material.



Transport

Hopping



Hopping conduction allows electrons to jump from one nanotube to another. Short contact lengths limit electrons from jumping back and forth.

To maximize conduction, Metallic Nanotubes are needed.

Alper Buldum and Jian Ping Lu, Phys. Rev. B 63, 161403 R (2001).

Program Goals: Conductor Size

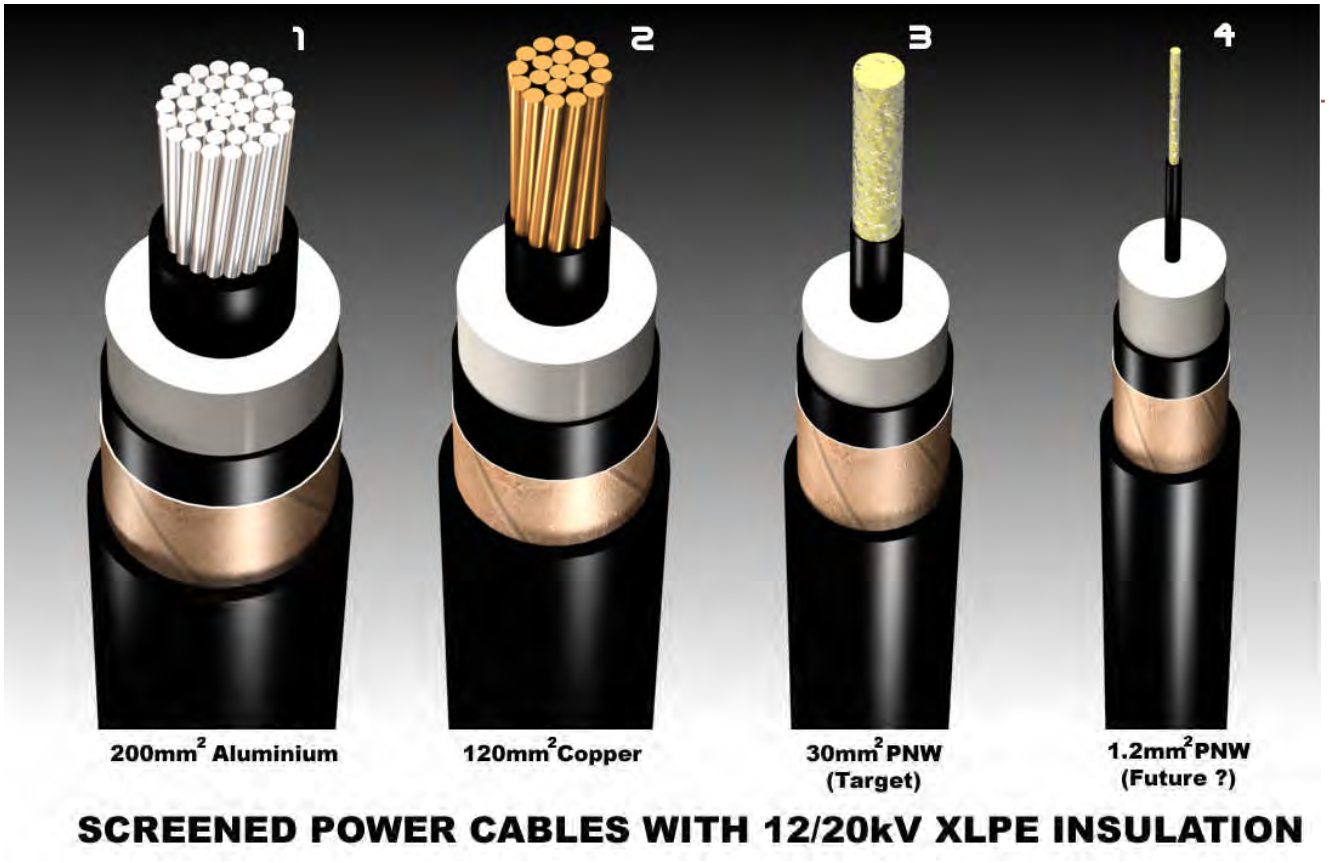


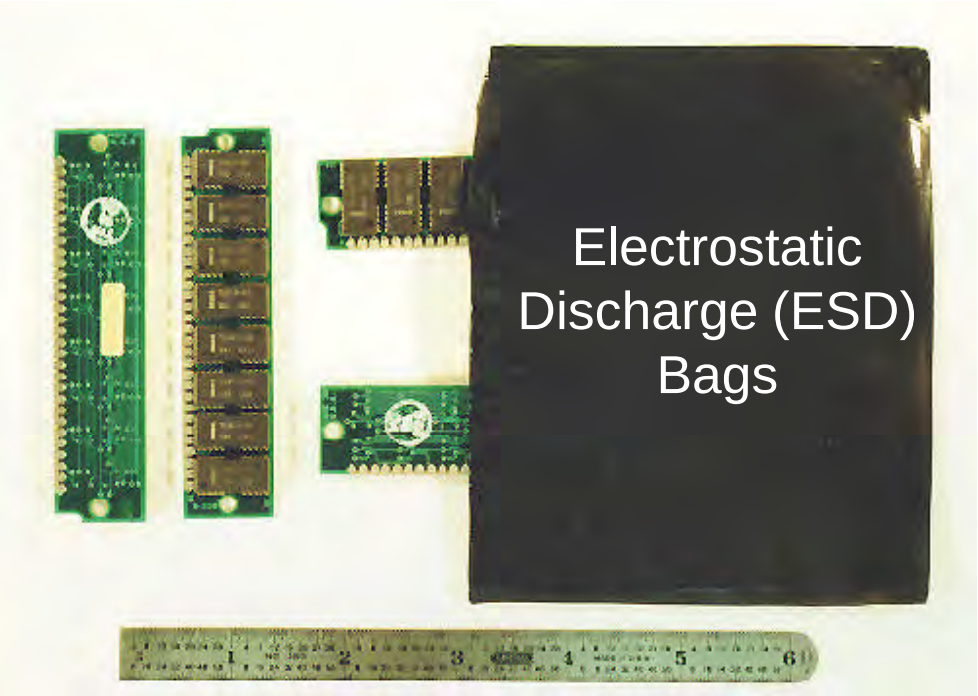
Table D.1.4.1	Cable 1	Cable 2	Cable 3	Cable 4
Cable (area) (mm^2)	200 (Al)	120 (Cu)	30 (PNU)	1.2 (PNU)
Mass in air (kg/m)	1.45	1.82	0.54	0.33
Diameter (m)	0.038	0.0327	0.0253	0.0195
Mass of displaced water (kg/m)	1.16	0.86	0.52	0.31
Weight in water (N/m)	2.820	9.406	0.242	0.234
Or (kg/m)	0.288	0.959	0.025	0.024

Picture compliments of Dave Madden

Background on Conduction: Polymer Nanotube Conductors: Pathway to a High Conductor

1996-1999: 13 to 14 orders of decrease in electrical resistivity.
1997-1999: Produced Electrostatic Discharge (ESD) materials.
2000: Produce multifunctional Nanotube Continuous Fibers (NCFs).
2002: Produced Electromagnetic Interference (EMI) Materials.
2005: Produced conducting wire.
2007: Produced Lightning strike protection.
2009: First Polymer Nanotube Umbilical (1 ft *Demonstration Sample*).

2009: 19 orders of magnitude decrease in electrical resistivity.

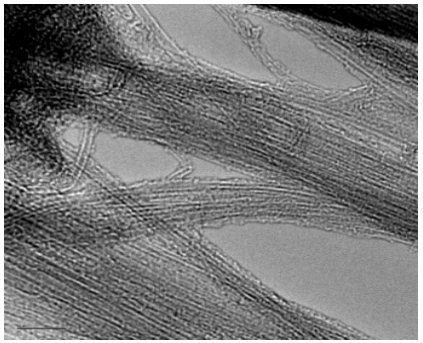


Demonstration Sample in 1999 showing an ESD bag that will hold computer parts. Bag showed rapid discharge in a range of relative humidities.

Status of Tasks and Goals as of December 10, 2009

Technical Tasks (Monthly)	Completion Date	Status
a. Obtain SWNTs & m-SWCNTs	May	Completed
b. Process wires w/polymer 1 & 2	April	Completed
c. Test properties of 1 & 2 wire	April	Completed
d. Characterize m-SWNTs	May	Completed
e. Conduct NT-NT study	September	In progress
f. Improve NT-NT conduction	September	Completed
g. Disperse SWNTs in 1 & 2	April	Completed
h. Disperse m-SWNTs in 1 & 2	October	Completed
i. Implement Electric Fields	November	Completed
j. Characterize NT filled wires	December	Completed
k. Conduct physical tests	December	In progress
l. Connection study	December	Completed
m. Reporting	Monthly	Completed
Milestones		
1. Obtain m-SWCNTs	March	Completed
2. Produce first 1 ft wire	June	Completed
3. Evaluate for umbilical	September	Completed
4. Evaluation & optimization	September	Completed
5. Optimize and prototype test	December	In progress
6. Final Report	December	Pending
7. nano-Umbilicals Workshop	December	In Progress

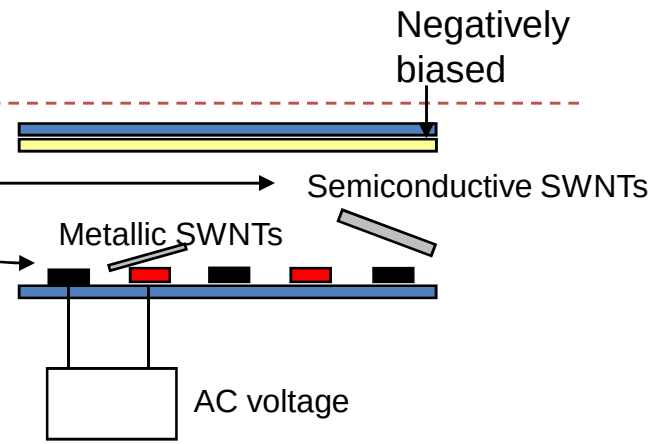
Process Schematic

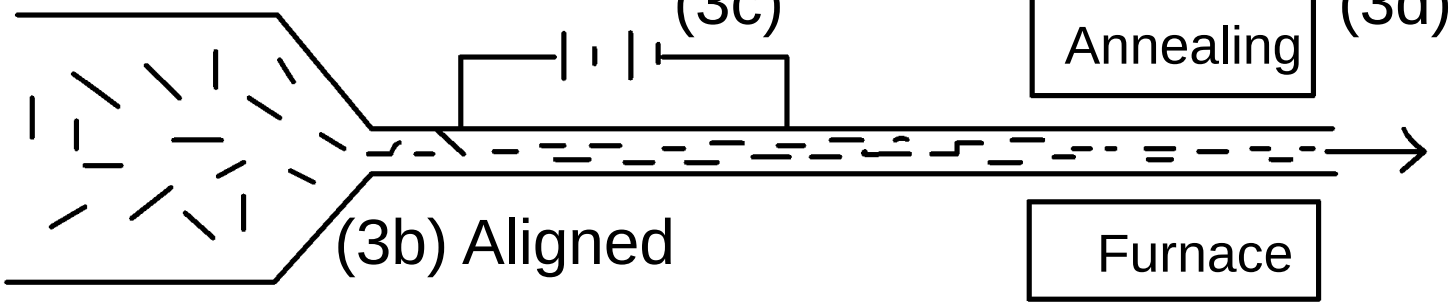


(1)

Semiconductors
Metallic

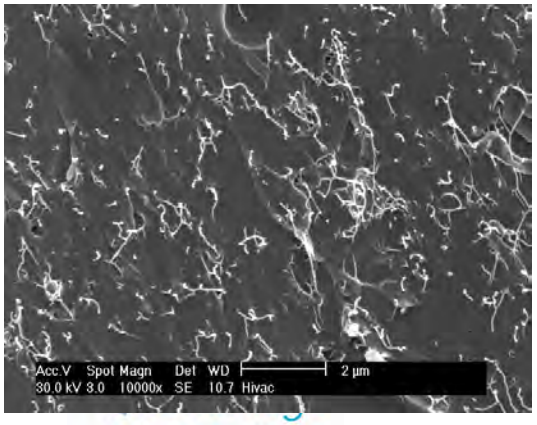
(2)

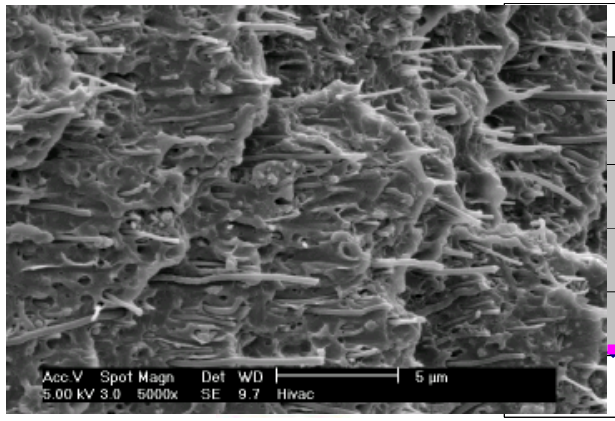


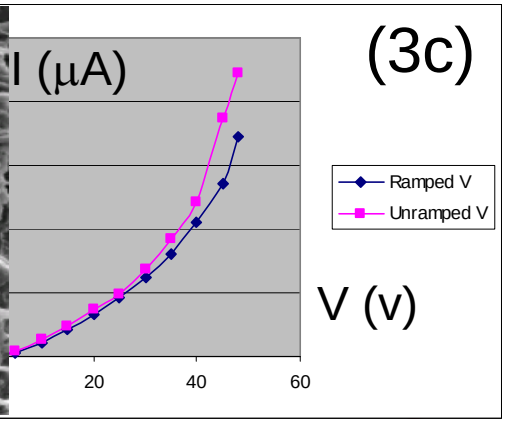


(3a)

(3b) Aligned







Our approach to build the proposed product

(1) Preparation (Purification) of starting nanotube material. ✔-

Further improved purification of m-SWNTs (two approaches)

(2) Separation of the metallic SWNTs.

Selected SWNTs with enhanced metallics (40% m-SWCTs) ✔-

(3) Processing into a polymer wire or tape.

(3a) Mixing in a polymer. ✔-

Increase nanotube content to 90 wt%. Used incipient wetting and the "Winey Method". Need to implement decanting.

(3b) Use of extrusion and/or elongational flow. ×+

Still need to further improve alignment.

(3c) Use of electric fields. ✔-

Need to find gap size and to shorten time.

(3d) Polymer Annealing. ✔-

Demonstrated improvement but need optimization process.

(3e) Optional: Deposition of metal contacts. ✔-

Demonstrated improvement but need to move to lager scale.

Advances have been made, next steps will bring more resistivity reduction.

NanoRidge RICE UNIVERSITY Technip DUCO Chevron

Example Samples Processed to Date

Composites	Wt% of NTs	Processing method
MWNTs/HDPE	5%	Dry mixing + Injection
MWNTs/HDPE	10%	Dry mixing + Injection
MWNTs/HDPE	15%	Dry mixing + Injection
MWNTs/HDPE	20%	Dry mixing + Injection
MWNTs/HDPE	5%	Dry mixing + Haake extrusion
MWNTs/HDPE	10%	Dry mixing + Haake extrusion
MWNTs/HDPE	15%	Dry mixing + Haake extrusion
MWNTs/HDPE	20%	Dry mixing + Haake extrusion
MWNTs/HDPE	5%	Incipient wetting + Dry mixing + Haake extrusion
MWNTs/HDPE	10%	Incipient wetting + Dry mixing + Haake extrusion
MWNTs/HDPE	15%	Incipient wetting + Dry mixing + Haake extrusion
MWNTs/HDPE	20%	Incipient wetting + Dry mixing + Haake extrusion
MWNTs/HDPE	5%	Dry mixing + Miniextrusion
MWNTs/HDPE	10%	Dry mixing + Miniextrusion
MWNTs/HDPE	15%	Dry mixing + Miniextrusion
MWNTs/HDPE	20%	Dry mixing + Miniextrusion
MWNTs/HDPE	30%	Dry mixing + Miniextrusion
MWNTs/HDPE	40%	Dry mixing + Miniextrusion
MWNTs/HDPE	50%	Dry mixing + Miniextrusion
MWNTs/HDPE	60%	Dry mixing + Miniextrusion
CG NTs/HDPE	10%	Winney sample + Injection
CG NTs/HDPE	10%	Winnery sample + Miniextrusion
MWNTs/MDPE	5%	Dry mixing + Haake extrusion
MWNTs/MDPE	10%	Dry mixing + Haake extrusion

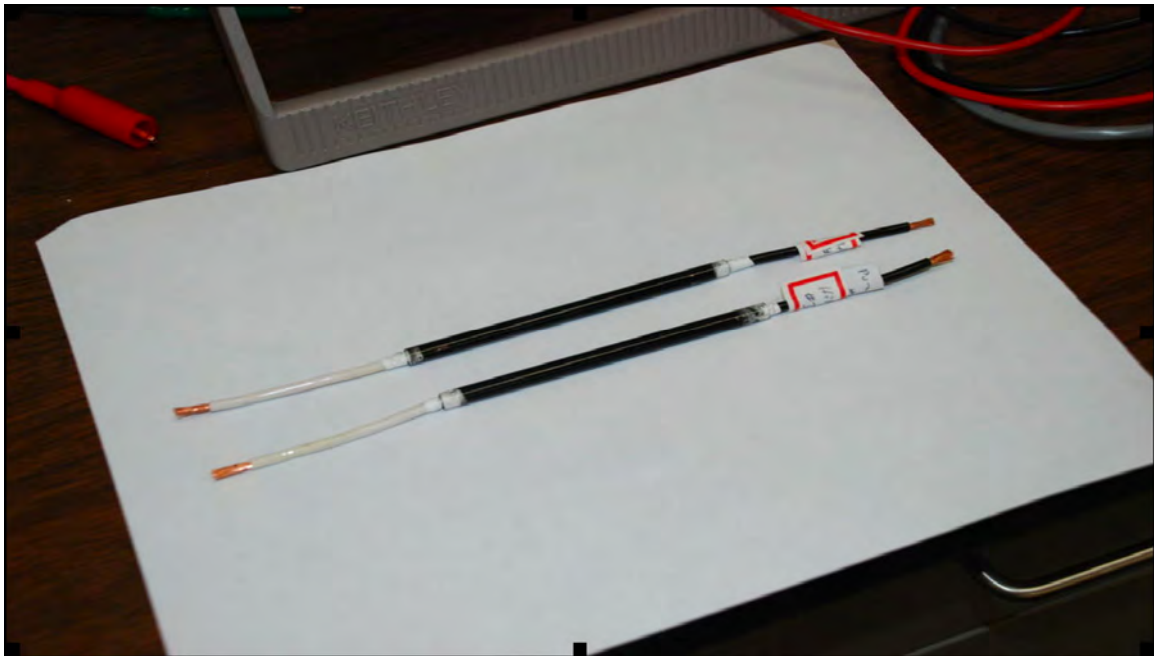
Three melt processing approaches are being used:

- Injection molding (up to 6 grams)
- Mini-extrusion (10 grams)
- Haake extrusion (100 grams).

Wt%s from 5 to 60 are being processed. Typical concentrations are 10 wt%.

Outcomes: Polymer Nanotube Umbilical

A PNU Test sample configuration where a number of the processing conditions are used.



Processing Tasks

h: Dispersion

i: Electric Fields

b: Annealing

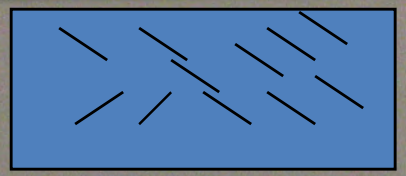
A Dymex polymer (thermoset) is shown here.

A method to produce the test sample to a one foot length has been identified and is currently being considered (Proprietary).

Outcomes: Produce 1st One Foot Wire

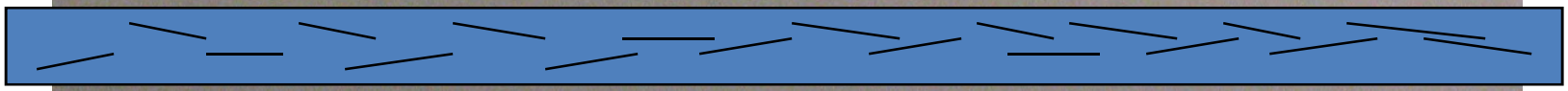
PE w/10 wt% SWNTs/Processed by melt spinning.
Various diameters have been produced with smaller diameters being more optimal at this time.

A PNU wire is shown below which exceeds one foot in length.
A number of the processing tasks were used: a, b, f, g, h, i, and l.



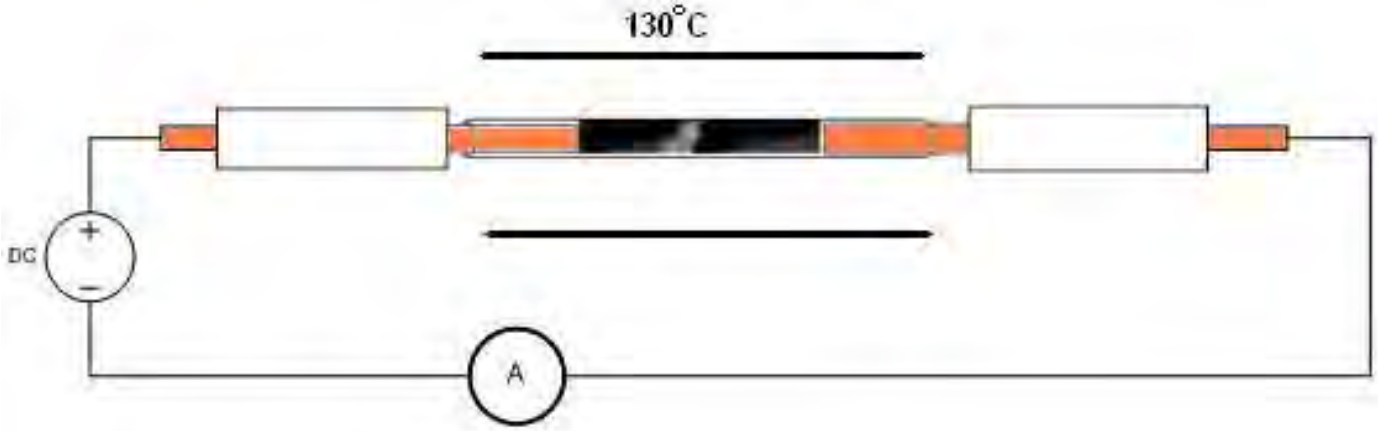
Explanation for thinner wire, better conductivity

Keep the same volume, 1/2 diameter, ¼ cross section area, 4 x length



Better alignment in uniaxial direction

Current method for implementing the electric field



- 4 samples (MDPE + 10 wt% SWNTs) were tested.
- Samples required 4 ~ 5 rounds of conditioning, before it starts conducting well.
- Conditioning rounds were reduced with improvements made to the test sample.

- The best samples carried a current of close to 16 amps for 2 V.
- The distance between the leads for the best sample is close to 0.7-7.62 cm.
- Specific resistivity was 2.1 * 10^{-2} ohms / sq cm

Nanotube Conductivity

http://www.nano.gov/html/news/SpecialPapers/Nanotubes%20For%20Power%20Transmission%20Line%20MaterialsA.htm.
This reference cites the following:

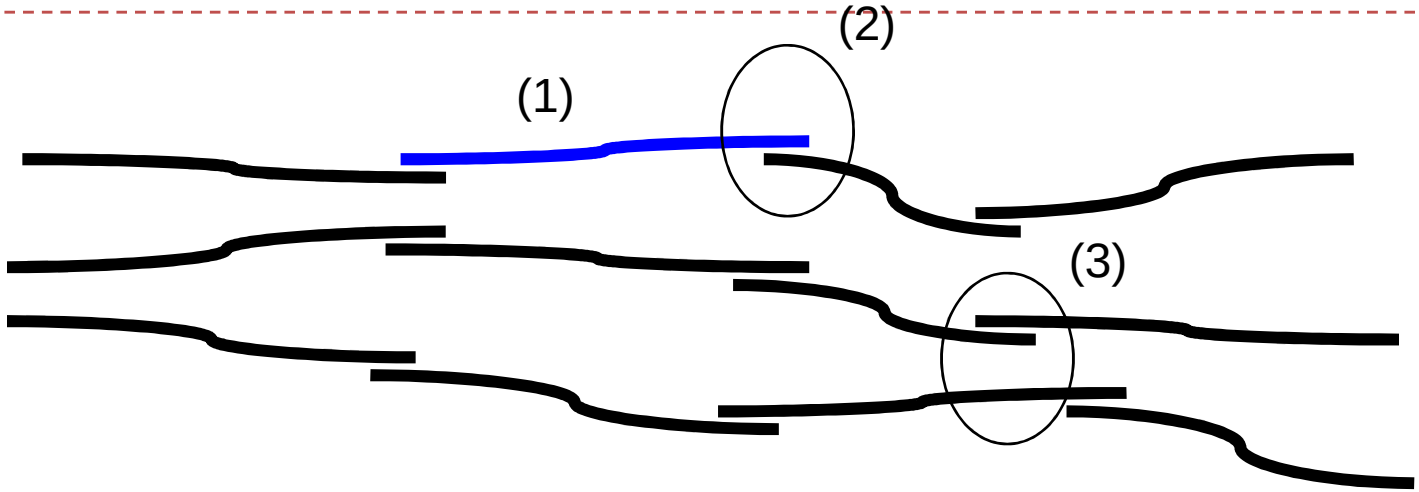
"This high conductivity derives from the highly efficient transmission of electrons down the individual tubes acting as quantum wave guides in one direction, and the efficient resonant quantum tunneling of the electrons from tube to tube as the current passes down the fiber."

Several researchers have demonstrated that one single wall carbon nanotube can carry currents up to **20 microamperes**.

Concerns

1. Starting purity plays a role.
2. Obtaining separated nanotubes.
3. Level of disentanglement plays a role.
4. Nanotube type is important for two reasons.
   - Probabality of metallic to metallic plays a role.
   - Nanotube to Nanotube contact is important.
   - (S to M (10^0), S to S (10^1), M to M (10^3)
5. Properties produced in the laboratory are not what can be produced in manufacturing.
   - Ropes vs. single nanotubes plays a role.
   - Polymer between the nanotubes plays a role.
     - Wire diameter plays a role.
5. Conditions of the electric fields play a role.
6. Final annealing plays a role.

Background: Directed Nanotube Network (DNN)



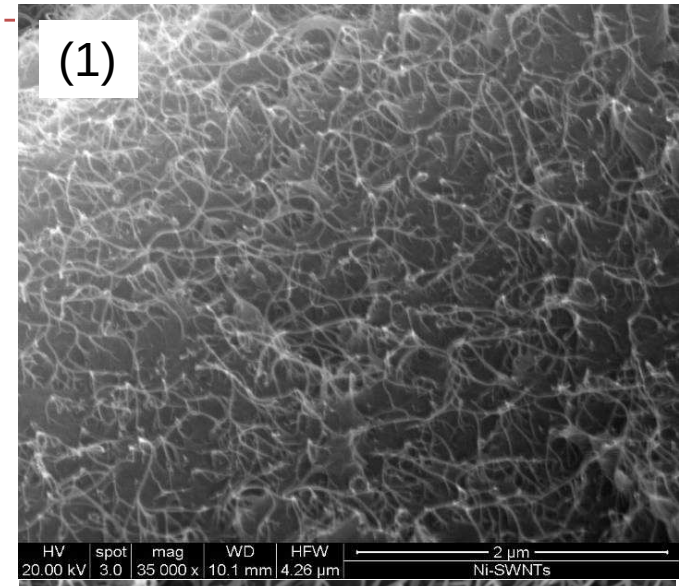
A schematic depicting a network of (1) m-SWCNTs that are arranged to promote maximum electrical conduction. The network is made up of (2) connected nanotubes that provide for *ballistic transport* along the nanotube length and *resonant quantum tunneling* from one nanotube to the other. Gap distances between the various chains prevent electron hopping from one pathway to the next. m-SWCNTs may vary in length but the (3) connections will be optimized for low contact resistance.

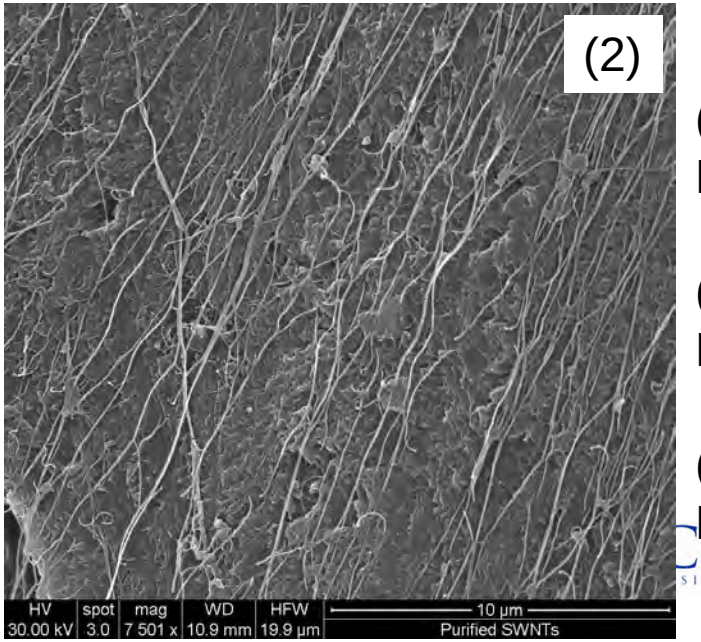
Nanotubes are nanometers (1.4nm) in diameter and microns in length.
Electrical conduction is as high or better than copper.
Mechanical properties include: UTS: ~50-150GPa/Elastic Modulus: 1 TPa

Disperse m-SWNTs

The Winey method for dispersion:
A version of the Incipient Wetting method where the following is used:

1) SWNTs are dispersed in Dichlorobenzene and sonicated. 2) After 3 hours, the temperature of the SWNT + DCB is raised to 110C. In a different beaker MDPE is dissolved in DCB at 110C. 3) The DCB + MDPE solution is added to the SWNT dispersion. 4) The mixture is placed in a ice bath and sonicated till the temperature reached below 70C. 5) The mixture is then vacuum filtered and dried.

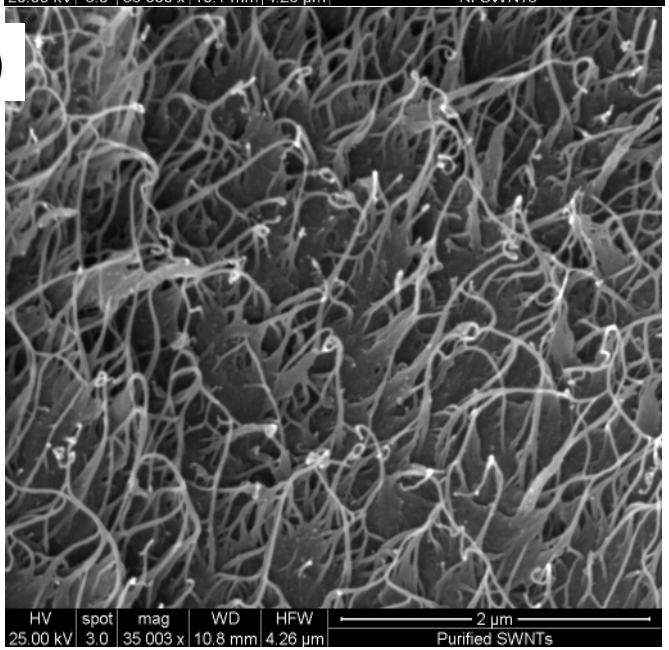




(1) After Winey Method.

(2) After electric Field applied.

(3) After electric Field applied.



Improving Percentage of Metallic Nanotubes

(2) Higher percentage m-SWNTs ensures similar type NT-NT contacts. Current nanotube compositions have some metallic to semiconductor contacts (not optimal contacts).

With unseparated nanotubes:

First nanotube is metallic	(1/3 chance is metallic)
Second nanotube is metallic	(1/3 chance is metallic)
Chance of metallic to metallic:	(1/9)

With current sorted nanotubes:

First nanotube is metallic	(2/3 chance is metallic)
Second nanotube is metallic	(2/3 chance is metallic)
Chance of metallic	(4/9 chance, improved by 2)

With proposed enhancement:

First nanotube is metallic	(8/9 chance is metallic)
Second nanotube is metallic	(8/9 chance is metallic
Chance of metallic	(64/81 chance, improved by 7)

The Role of Concentration and Shear

High Mechanical Performance Composite Conductor: Multi-Walled Carbon Nanotube Sheet/Bismaleimide Nanocomposites By Qunfeng Cheng, Jianwen Bao, JinGyu Park, Zhiyong Liang,* Chuck Zhang, and Ben Wang, Adv. Funct. Mater. 2009, 19, 1–7.

"Applying mechanical stretching and prepregging (pre-resin impregnation) on initially randomly dispersed, commercially available sheets of millimeter-long MWNTs leads to substantial alignment enhancement, good dispersion, and high packing density of nanotubes".
"The nanocomposites demonstrate high electrical conductivity of 5 500 S cm^{-1} along the alignment direction". Concentration of nanotubes was 60 wt% MWNTs.

High concentrations and shear can enhance conduction conditions.

Electric Field Specifications

A review and analysis of electrical percolation in carbon nanotube polymer composites Wolfgang Bauhofer, Josef Z. Kovacs,
Composite Science and Technology, 69 (2009) 1486-1498.

Review of 121 papers on electrical properties.
Results from the review:
(1) Dispersion is very important.
(2) Entanglements reduce conductivity (up to 50 times (MWNTs))
(3) Electric fields align nanotubes and enhance attractive forces between nanotubes.

400 x 10^{-6}m (0.4 mm) separation between electrodes for electric field use.

Electric Field Alignment

Electric-field assisted assembly and alignment of metallic nanowires
Peter A. Smith, Christopher D. Nordquist, Thomas N. Jackson, and Theresa S. Mayera, *Benjamin R. Martin, Jeremiah Mbindyo, and Thomas E. Mallouk*

"This letter describes an electric-field assisted assembly technique used to position individual nanowires suspended in a dielectric medium between two electrodes defined lithographically on a SiO2 substrate. During the assembly process, the forces that induce alignment are a result of nanowire polarization in the applied alternating electric field. This alignment approach has facilitated rapid electrical characterization of 350- and 70-nm-diameter Au nanowires, which had room-temperature resistivities of approximately 2.9 and 4.5 x 10- 6 ohm cm".

(5 micron wide electrodes)

http://research.chem.psu.edu/mallouk/articles/APL01399.pdf

Electric Field Alignment

Aligned Single-Wall Carbon Nanotube Polymer Composites Using an Electric Field CHEOL PARK, JOHN WILKINSON, SUMANTH BANDA, ZOUBEIDA OUNAIES, KRISTOPHER E. WISE, GODFREY SAUTI, PETER T. LILLEHEI, JOYCELYN S. HARRISON, Journal of Polymer Science: Part B: Polymer Physics, 44 (2006) 1751-1762.

Use of electric fields 0.03 wt% Hipco.

Electrodes placed at a separation distance of 2.3 mm. In the electric field for 10 minutes. 10^{-6} S/cm

Self-Assembled Linear Bundles of Single Wall Carbon Nanotubes and Their Alignment and Deposition as a Film in a dc Field Prashant V. Kamat, K. George Thomas, Said Barazzouk, G. Girishkumar, K. Vinodgopal, and Dan Meisel†.
5 mm apart.
"When a dc voltage of ~40 V was applied, we observed a slow movement of carbon nanotubes from the suspension toward the positive electrode".

Tunneling

Dominant role of tunneling resistance in the electrical conductivity of carbon nanotube–based composites Chunyu Li, Erik T. Thostenson, and Tsu-Wei Chou,
Applied Physics Lett. 91 (2007) 223114-1 to 223114-3.

Maximum tunneling distance is found to be 1.8 nm.

"Electrical conductivities of composites with in plane random distributions of carbon nanotubes follow the scaling law and the critical exponent depends on the level of contact resistance".

"It is also noted that the extrapolation of the EC of CNT networks without insulating layers at 100% content gives about 7.2 - 10^5 S / m, which is very close to the conductivity of 10^6 S / m of individual CNTs we used".

Conduct NT-NT Study/Improve NT-NT Connection

Three Approaches: (1) Zyvex manipulation
(2) Ames Interdigitized Sample
(3) Use of Focused Ion Beam Equipment
(4) Doping

Use of Focused Ion Beam Equipment

IPICyT in San Luis Potoci, Mexico has equipment for conducting high sensitivity nanotube manipulation.

With this equipment we can imagine at the nanoscale, move nanotubes around, and create contact conditions for measuring electrical conductivity (NT-NT contact).

Experiments are being conducted to achieve samples of several nanotube conditions.

Conductivity of SWNT Networks

Electrical Conductivity of Single-Walled Carbon Nanotube Networks
P. N. Nirmalraj, P. E. Lyons, S. De, J. N. Coleman, and J. J. Boland, Nano Le (2009) 3890-3895.

“Transport in single-walled carbon nanotube networks is shown to be dominated by resistance at network junctions which scale with the size of the interconnecting bundles”.

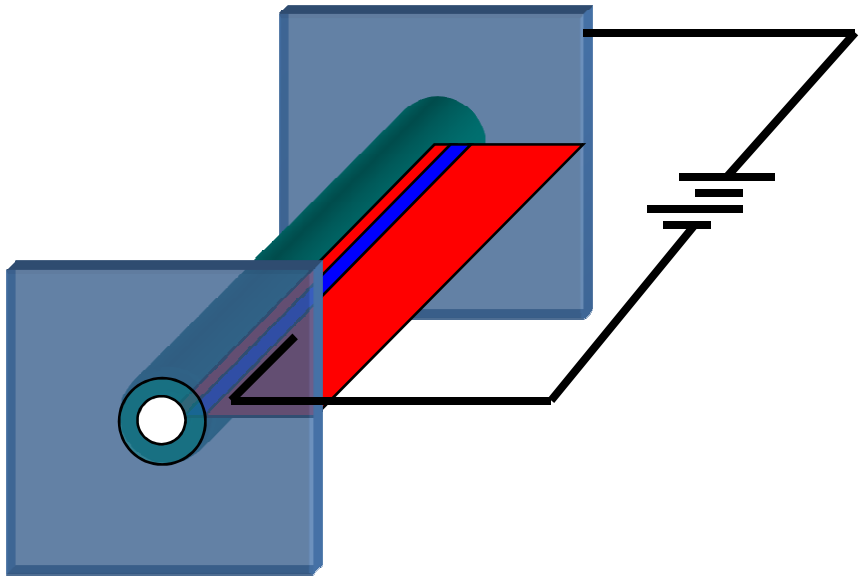
“Acid treatments that dope the individual nanotubes produce a dramatic reductionin junction resistance.

Smallest resistances occurs between individual nanotubes.

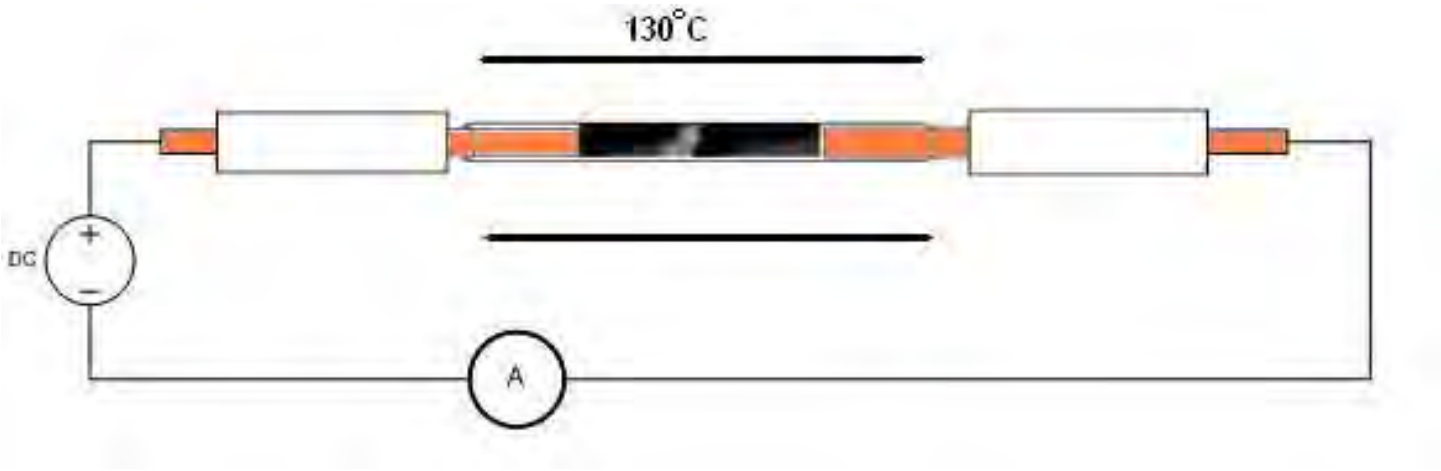
Implement Electric Fields

Design of an Electric Field Fixture:

1. Separated parallel plates with a hole in the middle so the PNU can go through.
2. A tube is placed in the holes so that a heating element can be put around the wire.



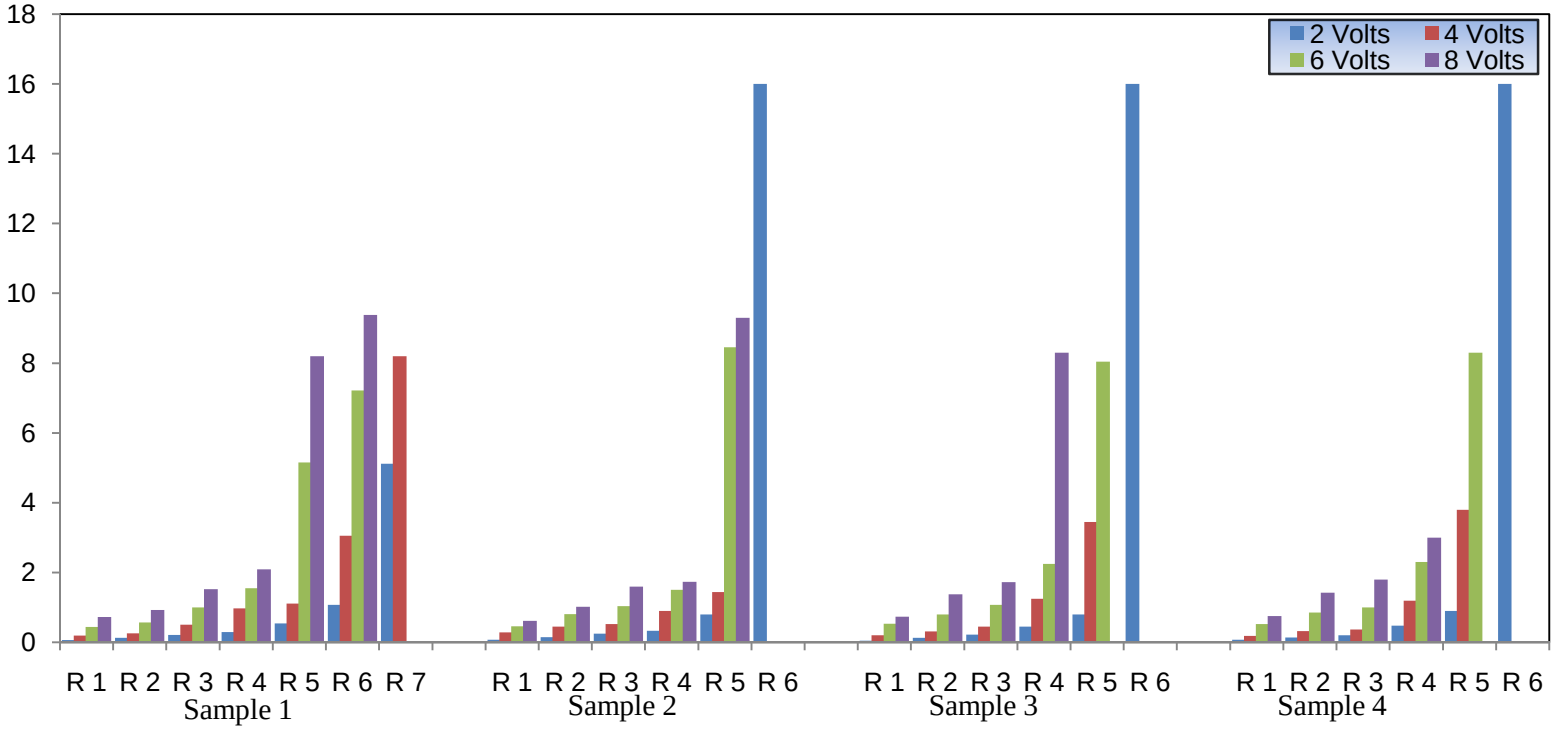
Current method for implementing the electric field



- 4 samples (MDPE + 10 wt% SWeNTs) were tested.
- Samples required 4 ~ 5 rounds of conditioning, before it starts conducting well.
- The best samples carried a current of close to 16 amps for 2 V.
- The distance between the leads for the best sample is close to 0.7 cm.
- Specific resistivity was 2.1 * 10^{-2} ohms / sq.cm
- Current samples require conditioning (more than one melting pass).

Evaluation & Optimization

Target: 500 amps at the same voltage for the copper conductor.
Proposed: (a) Stranded wire (19 strands) or (b) Solid Core wire.
For stranded wire: On average ~26 amps to be carried by each strand.
Current Design and Evaluation: Single strand of SWNTs/PE.



Recent conditions may be limited by available power supply.

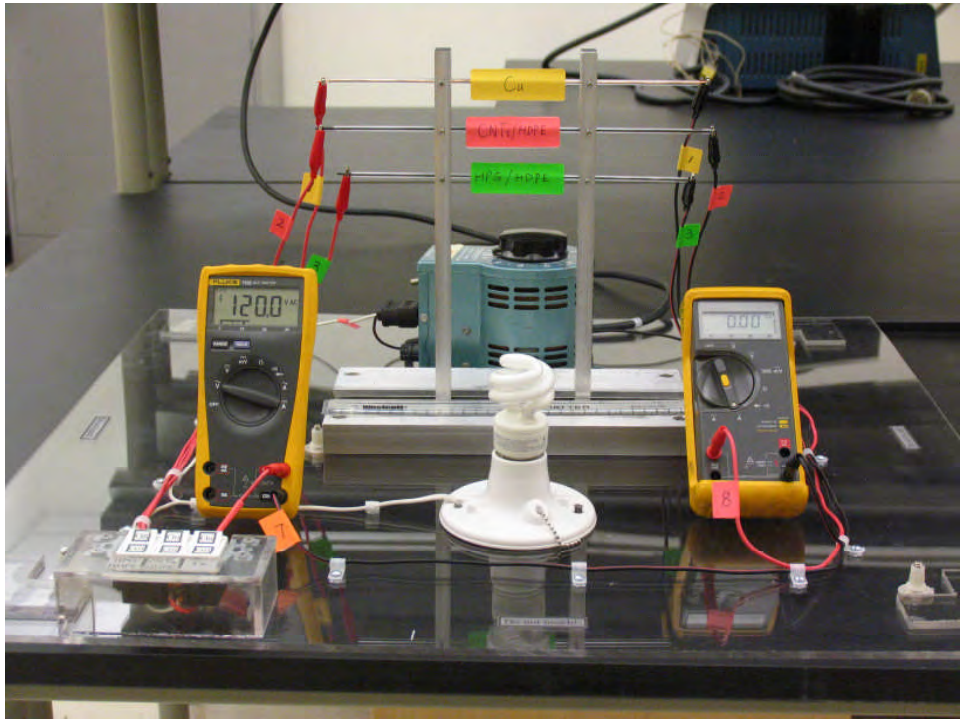
Samples for Resistivity Testing

Sample	Resistivity (ohm.cm)	Diameter (cm)	X-section area (cm^2)
Polyethylene (HDPE)	10^{17}	0.394 (~0.4)	0.12
10 wt% CG / MDPE	~ $1* 10^3$ – $1.5* 10^3$	0.394	0.12
10 wt% CG / MDPE (application of electric field) at room temperature.	~ $5 * 10^{-1}$ – 10	0.394	0.12
10 wt% purified Hipco / MDPE (application of electric field) at room temperature.	~ $2 * 10^{-1}$ – 5	0.394	0.12
10 wt% CG / MDPE (application of electric field) at high temperatures)	~ $4*10^{-2}$ – $6*10^{-2}$	0.394	0.12
10 wt% purified Hipco / MDPE (application of electric field) at high temperature.	~ $2*10^{-2}$ – $6*10^{-2}$	0.394	0.12

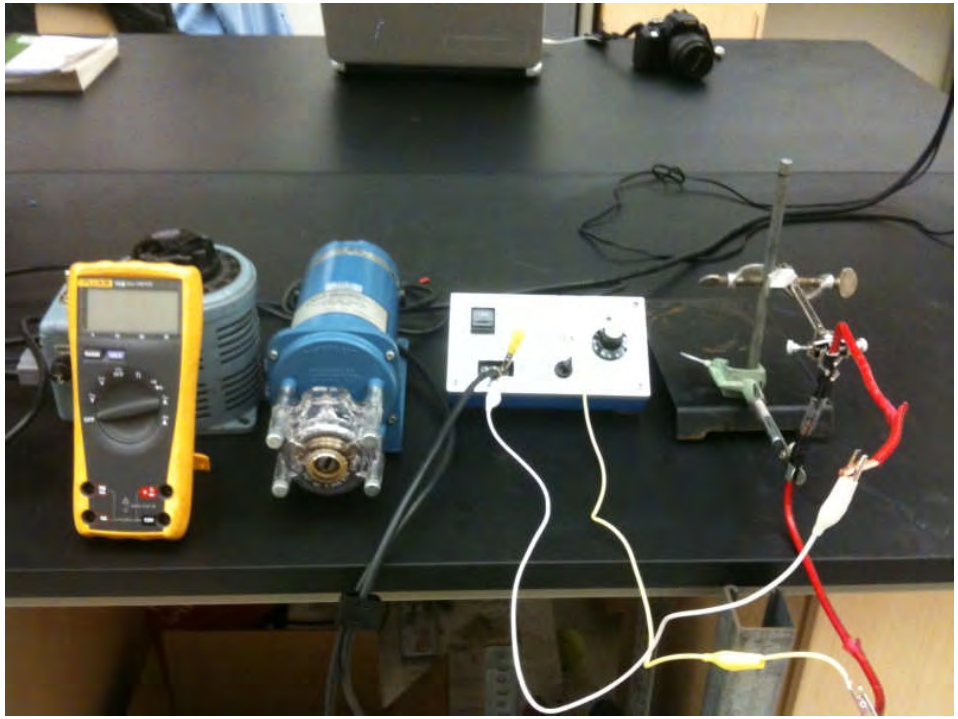
Sample	Resistivity	Diameter	X-section area
10 wt% p-Hipco, w/ single core lead	~ $7*10^{-2}$ - $9*10^{-2}$	0.394	0.12
10 wt% p-Hipco w/ smaller diameter	~ $4.5*10^{-1}$ - $8*10^{-1}$	0.2	0.03

Outcomes: Demonstrations

Two demonstration set-ups to show samples produced and conditions tested.



Set-up #1: Demonstration with a light Bulb. Comparisons.



Set-up #2: Demonstration with a Pump. Higher voltage condition.

Outcomes: What was Learned

Partial listing related to conduction (with a low concentration focus):

- Approach: Advance materials properties by adding nanotubes then **lower** concentrations to get even more advancements.
- Dispersing nanotubes in the polymer leads to conduction at **low** concentrations while segragated nanotubes in polymer do not enhance mechanical strength.
- Nanotubes dispersed in a polymer fiber enable handling aligned nanotubes for a range of applications at 0 to 100% concentrations.
- Synergism between various nanoconstituents leads to enhancements at **lower** concentrations than used by the individual additives.
- Nanotubes can act as templates for other nanoconstituents to promote multifunctionality at **low** concentrations.
- A Directed Nanotube Network (DNN) can produce high conduction while **low** concentrations of nanotubes can be used.

Outcomes: Talking Points

- Produced PNUs with nanotube concentrations up to 90 wt%.
- Polyethylene, Dyamx, and polystyrene were used as the polymers.
- The lowest resistivity value reached was $2*10^{-2}$ Ωcm.
- The highest voltage carried by the PNU was 40V (the limit has not been evaluated).
- The highest current carried by the PNU was 16 A (not fully optimized).
- Several new steps for lowering the resistivity have been identified.)

Outcomes: Supplemental Enhancements

- Enhanced purification
- Microwave heating (proprietary)
- Centrifugation (improved dispersion)
- Functionalization
- Annealing (proven improvements)
- Higher concentrations
- Doping Up to 100% improvement (Synergism)
- Enhanced NT-NT connections
- Retained polymer
- Stretching

Program Outcomes

1. One foot wire conductor produced.
2. High dispersion has been achieved by the “Winey” Method.
3. We have used electric fields and designed a fixture for process manufacturing.
4. We have produced a number of samples using the Dymax sample configuration. Early samples were produced with styrene. A number of samples have been processed by melt spinning.
5. A current carrying capability of 16 amps has been produced
6. where 26 A is needed..

   The sample was limited by the power supply used.

   More optimization is planned.
6. The workshop is being held on Ultra-High Conductivity Conductors.
7. The test wire is being demonstrated at the workshop.

Program Support: DOE RPSEA, Chevron