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The Characterization and Circumvention of Carbon Nanotube Junctions- The Route to Practical Carbon Conductors Through Extreme Frequency, Fields, and Light

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14. ABSTRACT
The three-year project focused on the influence of junctions between carbon nanotubes and ways of improving either electrical transport or bypassing junctions altogether. We found that conductivity improves with frequency for AC signals, an effect that can be improved by sorting for metallic or semiconducting concentrations. We also examined the effect of cryogenic temperatures and strong magnetic fields, and fund that chemical doping can enhance the carrier density and junction transport. Aligned CNT materials have delocalized charge carriers as opposed to the localized "hopping" of charge carriers in unaligned materials. Finally, high power laser treatment can help increase conductivity by a factor of ten.

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The Characterization and Circumvention of Carbon Nanotube Junctions- The Route to Practical Carbon Conductors Through Extreme Frequency, Fields, and Light

Dr Krzysztof K.K. Koziol and Mr John Bulmer

Abstract: The following summarizes research over the past three years in understanding the influence of junctions between carbon nanotubes (CNT) in a bulk CNT conductor and then discusses methodologies in either improving electrical transport across these junctions or bypassing the junctions all together. First, we look at the role of junctions with high frequency transport (up to 220 GHz) and see that conductivity improves with frequency as a result of bypassing CNT junctions with a capacitance effect. If the CNTs are sorted for metallic or semi-conducting concentrations, the conductivity increase with frequency is significantly greater. Next we move to DC transport under cryogenic temperatures (~1 K) and extreme magnetic field (~60 T). Although applications are more specialized in these environments, they show the various effects of junctions and generalized disorder on the transport. We find that chemical doping not only enhances the carrier density on the semi-conducting CNTs, but it improves the transport across junctions in general. We find that highly aligned CNT materials have charge carriers that are delocalized across the CNTs, opposed to a localized hopping mechanism found with unaligned CNT materials. Under extreme high fields, we see a new spin saturation mechanism which settles a disagreement found in literature concerning why CNT resistance increases in field. Finally, we show a high power laser post-treatment process decreases the impact of junctions on the transport. After the treatment of high intensity light, conductivity of the CNT material jumps a factor of ten and makes it optically transparent.

Introduction. The efficiency of carbon nanotube (CNT) based electrical cables is incrementally progressing with recent demonstrations of bulk CNT cables exceeding the conductivity of copper and aluminium on the basis of weight[1], competitive current carrying capacity[2], while simultaneously being mechanical strong[3]. These accomplishments are primarily a result of improvements in alignment, graphitic crystallinity, and purity, while there is some additional benefit to post process chemical doping. These advancements are exciting, but should be taken in historical context that the advanced carbon materials thirty years ago-- heavily doped polyacetylene (PAC)[4] and graphitic intercalation compounds (GICs)[5]– approached and exceeded copper's room temperature conductivity it its own right without weight considered. For both GIC's and PAC, crystallinity, purity, density, and alignment were paramount to achieving their performance. Today control of individual SWCNT length, alignment, and chirality is an evolving discipline and understanding its specific influences directs the development of SWCNT textiles with superior conductivity.

CNTs are themselves highly conductive and in measured, experimental situations exceed the conductivity of copper on an individual basis[6]. Putting billions and billions of CNTs together into a bulk textile, this ultra-high conductivity is lost. A majority of this loss comes from junctions between CNTs [7].

In this report, we will vary temperature, frequency, and ambient magnetic field in some of the most extreme manners available on the planet—and see the effects of transport on CNTs and the junctions between them. We will consider two primary CNT materials. The first are CNTs gathered in an unaligned manner into a "buckypaper." While unaligned, these CNTs are very pure and the concentration of metallic chiralities may be controlled exactly. The next material we will consider is aligned CNTs produced here at Cambridge. This material is less pure with amorphous carbon and residual iron catalyst. However the CNTs themselves are hundreds to thousands of times longer than in the case of the buckypaper. We will show recent progress in a post treatment laser process that greatly improves the crystallinity of these CNTs, as well as removes the amorphous carbon and iron catalyst. We show that these improvements increase the conductivity while simultaneously making it transparent. Considering recent advancement with CNTs and the achievements of older carbon materials thirty years ago, research into carbon conductors is a rich field of exploration and has immediate payoff in energy applications.

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[1] Zhao, *Scientific Reports* **1**,6 Sep 2011
[2] Wang, *Adv. Funct. Mater.* 24, pp. 3241–3249, 2014,
[3] Behabtu, *Science* **11** (3) pp. 182-186, January 2013
[4] Kaiser, *Advanced Materials*, 2001, Vol. 13 (12), 927.
[5] Inagaki, *Journal of Material Research*, 1989, Vol. 4 (6).
[6] Purewal, PRL **98,** 186808 (2007)
[7] Nirmalra, *Nano Letters*, 2009, Vol 9 (11), 3890.

High Frequency Transport. There have been a few routes suggested to overcoming extrinsic junction resistance to include making the CNTs longer and more aligned. Here we are considering high frequency transport. In a basic sense, charge carriers on one CNT oscillating on one CNT induce a current on another CNT. In a lumped parameter circuit model, the CNT junction is represented as a capacitor in parallel with a resistor (see figure 1). At a sufficiently high frequency, electromagnetic energy will travel across the capacitor and circumvent the resistor that creates heat. In the bulk material, this behavior manifests itself with a conductivity that increases with frequency. Note that this is opposite the behavior of most real world metals where conductivity decreases with frequency due to skin effect.

According to literature[8,9], CNT conductivity in general starts to improve starting in the microwave wavelengths. In this regime we wanted to test our CNT materials, which are unique due to the long length of the individual CNTs and their particularly high degree of crystallinity.

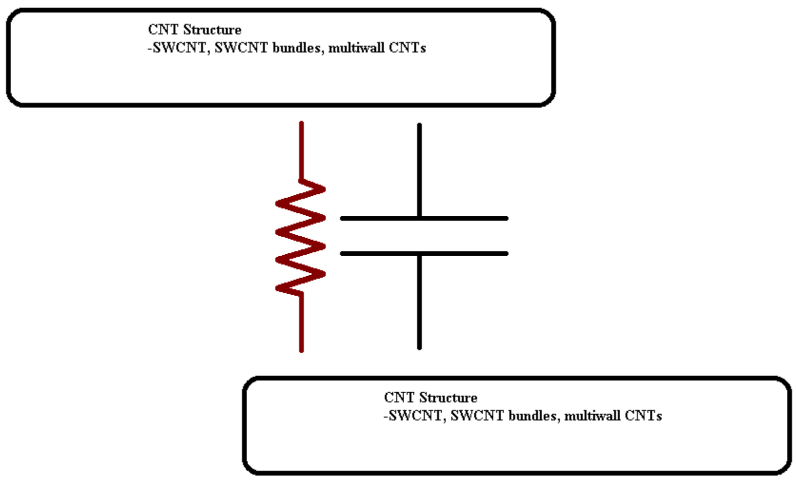


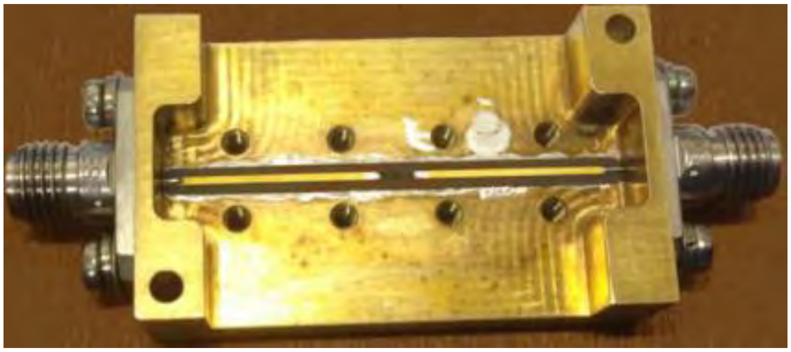
Figure 1. Lumped parameter model representing a CNT to CNT junction. A charge carrier may cross the junction by traveling through the resistor and generate heat, or at sufficiently high frequency may jump across via the capacitive effect.

At microwave wavelengths, the shape of the conductor and the return path are as important as the bulk material properties. We started with micro-strip, a simple type of electromagnetic waveguide which is precision manufactured by microwave specialists. CNT films were cut with laser cutters to exact specification and inserted into the micro-strip central conductor. The micro-strip was then connected to a vector network analyzer (VNA) that sends radar waves at various frequencies through the micro-strip and measures both the reflected and transmitted

[8] Hua, Applied Physics Letters, 90, pp.183119 (2007).

[9] Bulmer, *Scientific Reports* **4**, 3762, 2014.

signal. Computer modeling with Microwave Office turns these measured reflection and transmission coefficients into a frequency dependent conductivity.



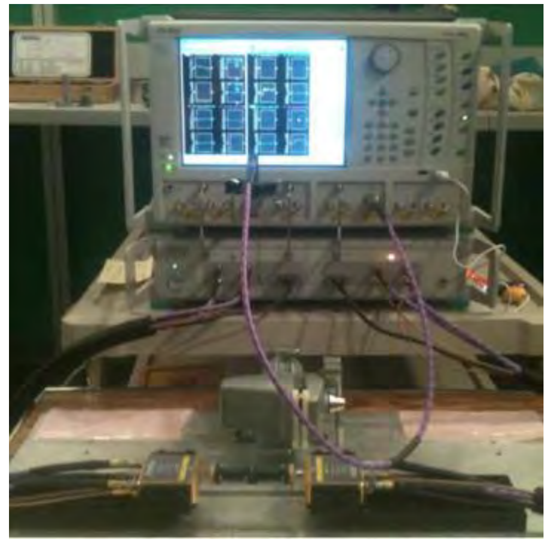


Figure 2. Left| Microstrip waveguide with various CNT types imbedded into the central conductor. **Right|** All microwave and millimeter measurements are conducted with a vector network analyzer (VNA) that transmits an incident electromagnetic wave at some frequency, and measures the transmitted and reflected signals.

Frequency dependent conductivity results are shown in figure 3. We see that CNTs composed of predominantly metallic conductivity increases with frequency at a greater rate than the other CNT materials. CNTs sorted for metallic chiralities is a new and emerging material and this is likely the first demonstration of a waveguide constructed from sorted CNT materials. This measurement technique however is limited to about 10 GHz and other techniques are required to probe higher frequencies.

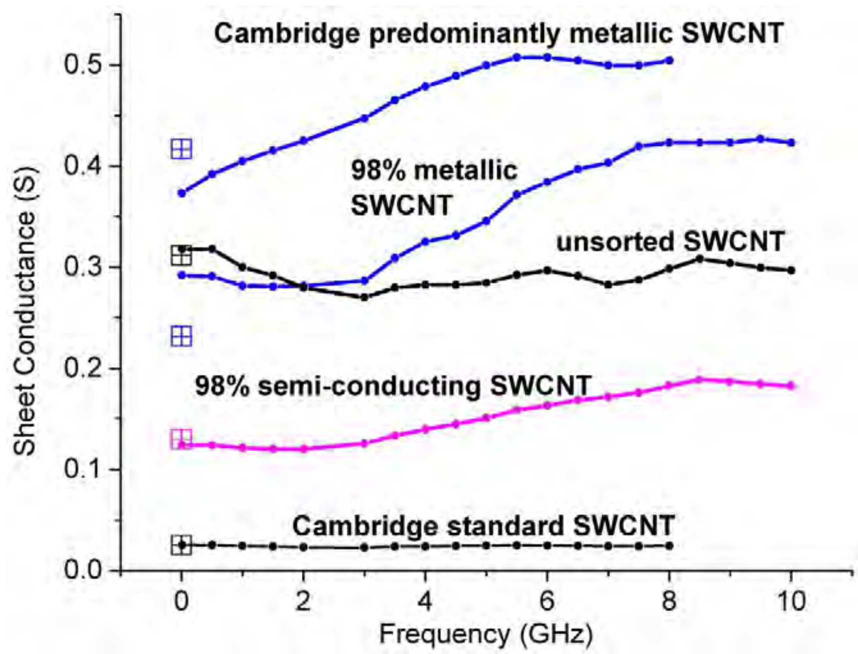


Figure 3. Sheet conductance of the CNT films embedded in the micro-strip waveguide. Films composed of primarily metallic concentrations increase in conductivity more than other CNT types.

To evaluate a higher frequency range, we next placed CNT films into rectangular waveguides. This technique will extend our microwave measurements into the millimeter wave regime, where the wavelength of the electromagnetic oscillation approaches the length of the individual CNTs (approximately 1 mm). The films were orientated such that they are perpendicular to the incident electromagnetic wave. Again, the sorted CNT material shows greater conductivity frequency dependence then the typical unsorted material (See figure 4). In particular, a film composed of predominantly semi-conducting CNTs also shows a significant frequency dependence with conductivity. Several studies model the frequency dependence of CNT conductivity with a universal disorder model. However, our results fit better to a generalized Drude model that has, until now, only been applied to CNT for the THz regime of the spectrum. The generalized Drude model is:

$$\sigma(\omega) = \frac{\varepsilon_0 {\omega_p}^2 \tau_s}{(1 - i\omega\tau_s)}\left(1 + \frac{c}{(1 - i\omega\tau_s)}\right) \qquad (1)$$

with ε_0-- the vacuum permittivity, ω_p-- the plasma frequency, τ_s-- the average carrier scattering time between charge carrier collisions, and c is the "persistence of velocity" or backscatter parameter with $-1 \leq c \leq 0$. When c= 0, this becomes the traditional Drude model and no charge carriers are backscattered. When *c* = -1, this means all charge carriers are localized and completely backscattered. As illustrated, this model allows us to extract a carrier density and relaxation time for CNT material as given in the following table.

	$\omega_p/2\pi$ (THz)	*Mfp(μm)*	*C*	DC cond. (kS/m)
98% metallic NI Adjusted R^2: 0.97	38.20 +/- 0.10	0.71 +/- 0.02	-0.84 +/- 0.00	83.5+
Unaligned SWCNTs[10]	33	3.2	0	69
98% semi- conducting NI Adjusted R^2: 0.99	159.2+/- 65.7	0.18 +/-.05	-0.98 +/-.01	26.8
93% Metallic SWCNT[28]	60.16	.054	-0.87	15.4
Unsorted NI Adjusted R^2: 0.97	6.72 +/- 0.08	1.0 +/- 0.02	-0.87 +/-0.00	5.4
Unaligned 94% semi-conducting SWCNT[11]	64	0.04	-0.69	1.8

Table 1. Quality control parameters as given by the generalized Drude model-- Plasma frequency ω_p, which is related to carrier density, Mean free path (*MFP*), and the degree of localization *c* . Measured values in this study are in red and in black are reported values on related materials from THz time domain spectroscopy.

[10] Hilt, O *Phys. Rev. B* **61**, R5129-R5132 (2000).

[11] Beard, M., *Nano Lett*. **8**, 4238-4242 (2008).

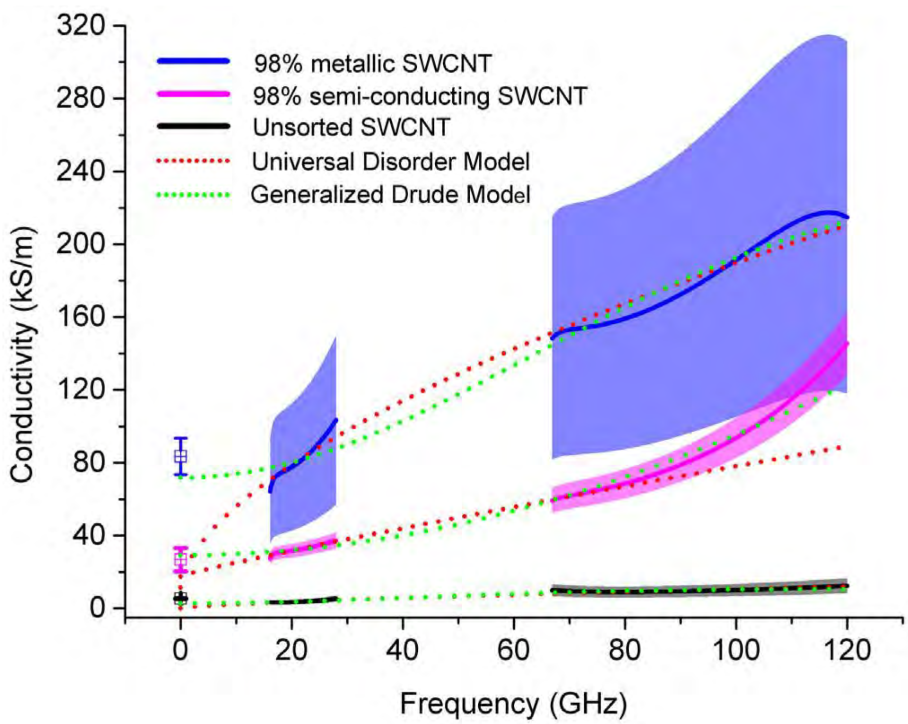


Figure 4. CNT film conductivity up to 120 GHz. Films composed of sorted CNTs show a much stronger dependence on frequency then the typical unsorted films.

Very recently we explored the conductivity of Cambridge CNT material with the rectangular waveguide technique up to 220 GHz. As shown in the far end of the spectrum (See figure 5), resonant behavior appears in a very consistent manner and is likely a result of the wavelength approaching the length of the individual CNTs. More research is required for verification and is the current focus of my work at the moment. However the hope is that this millimeter wave measurement will be key into characterizing the CNT material.

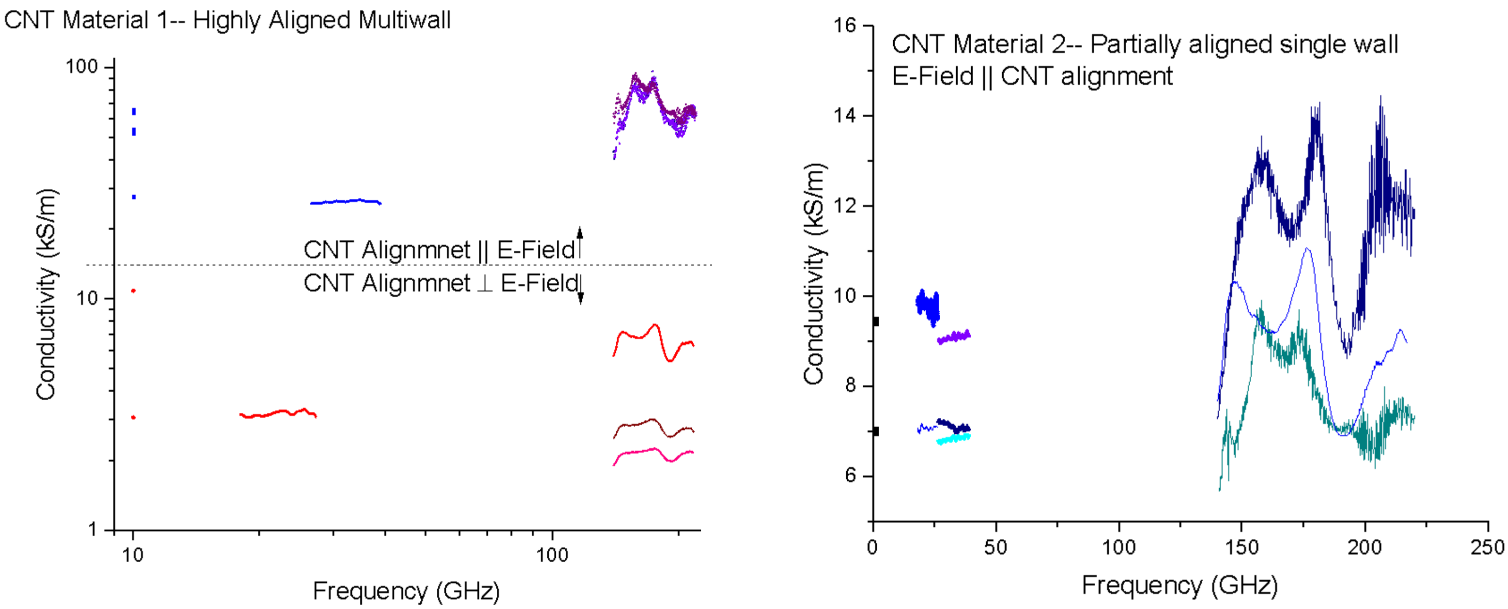


Figure 5. Preliminary results showing the conductivity of highly aligned CNT materials up in the millimeter wave regime. There appears to be a resonance as indicated by the fluctuation in conductivity. More experiments are currently underway.

The conductivity of CNT textiles improves with frequency. This behavior will be important for quality control to determine things like carrier density and CNT length. It is also important for applications. We demonstrated the first wave guide composed of CNTs of sorted chiralities. In addition, field emission is one of the few applications where CNTs outperform other materials without any caveats. As a possibility, we can imagine radar horn antennas operating in the microwave regime with peak to peak voltages around 1 kilovolt. This should be sufficient in creating pulsed electron sources from the CNTs while taking advantage of their frequency dependent conductivity.

DC transport in Extreme Temperatures and Fields. In the previous study we swept through frequency and measured the response of conductivity. Now we will focus on DC transport, but instead sweep the temperature and the ambient magnetic field. Temperature and magnetic field dependence sheds light on how charge carriers move through the CNT conductors and across their junctions. There are a few models that describe this behavior. One such model, variable range hopping (VRH), is where localized electrons hop for one location to another (for very disordered CNT materials). Another possible transport model is fluctuation induced tunneling (FIT) where electrons are delocalized across individual CNTs and loose energy as they jump the gap across CNT junctions. First we show the resistometry platform that measured the resistance of the CNTs as a function of temperature during the first year of study. Figure 6 shows the resistometry platform setup and figure 7 shows a typical resistance versus temperature measurement. The top left side of the curve in figure 7 shows a resistance minima where there are both metallic ($dR/dt>0$) and semi-conducting contributions ($dR/dt<0$). This extrinsic semi-conducting behavior is from the CNT junctions and the intrinsic metallic behavior are from the CNTs themselves. To improve the conductivity of the material, we need to decrease the contribution from junctions and this means making the minimum in resistance shift as far to the left as possible. For the most part, our Cambridge CNTs are too conductive and the resistometry platform, limited to temperatures above liquid nitrogen, would only show the resistance minima when the CNTs have been put in an un-doped/ annealed state. What is required is a system to go to liquid helium temperatures.

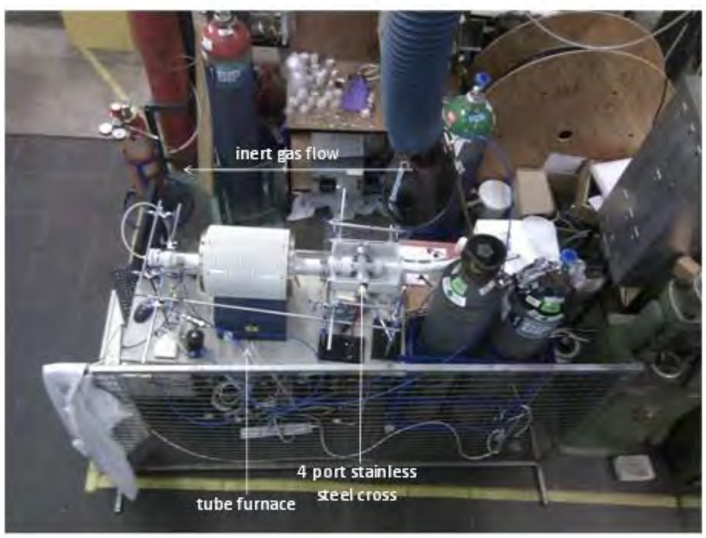


Figure 6. Resistometry platform built early on to measure resistance versus temperature. Unfortunately, it did not get cold enough to resolve the various transport mechanisms.

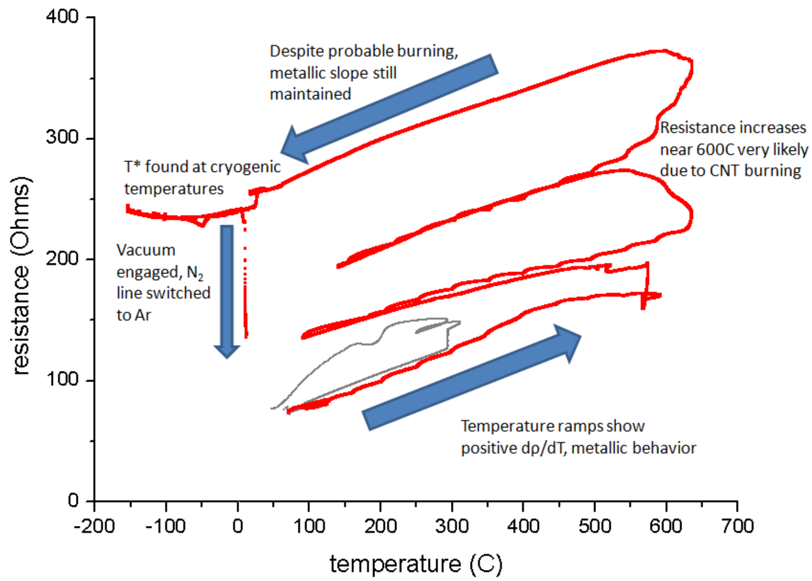


Figure 7. A typical resistance versus temperature plot made by the early resistometry platform. The resistance minima only appears after the sample has been degassed/ de-doped.

We realized colder temperatures were required to uncover the various transport mechanisms and we moved to a liquid helium system. Figure 8 shows resistance versus temperature measurements in liquid helium of unaligned CNT materials of either the typical unsorted variety or predominantly metallic chiralities. The unsorted SWCNTs follow 2D variable range hopping and the 95% metallic SWCNTs follow 3D variable range hopping. Doping with nitric acid improves the conductivity of both unsorted and metallic varieties and now both follow a power law, indicating a metal to insulator (M-I) transition. A M-I transition is where the localization lengths associated with the localized electrons stretch to infinity and the material is no longer an insulator. While doping unlikely affects the metallic SWCNTs themselves, chemical treatment with powerful acids also enhances junction conductivity and explains the drop in overall metallic SWCNT resistance after the nitric acid treatment. The most conductive sample is the doped unsorted SWCNT film– likely because after sufficient doping, semi-conducting SWCNTs act metallic and the unsorted film, on average, has twice the individual SWCNT length.

Shown in figure 9 is CNTs produced specifically at Cambridge. Here we see that the resistance minima is approximately 100 K, which is well below what the initial resistometry platform can measure. This data fits bets to fluctuation induced tunneling where electrons are delocalized across the CNT, but must tunnel through small resistive barriers to conduction (in this case the CNT junctions).

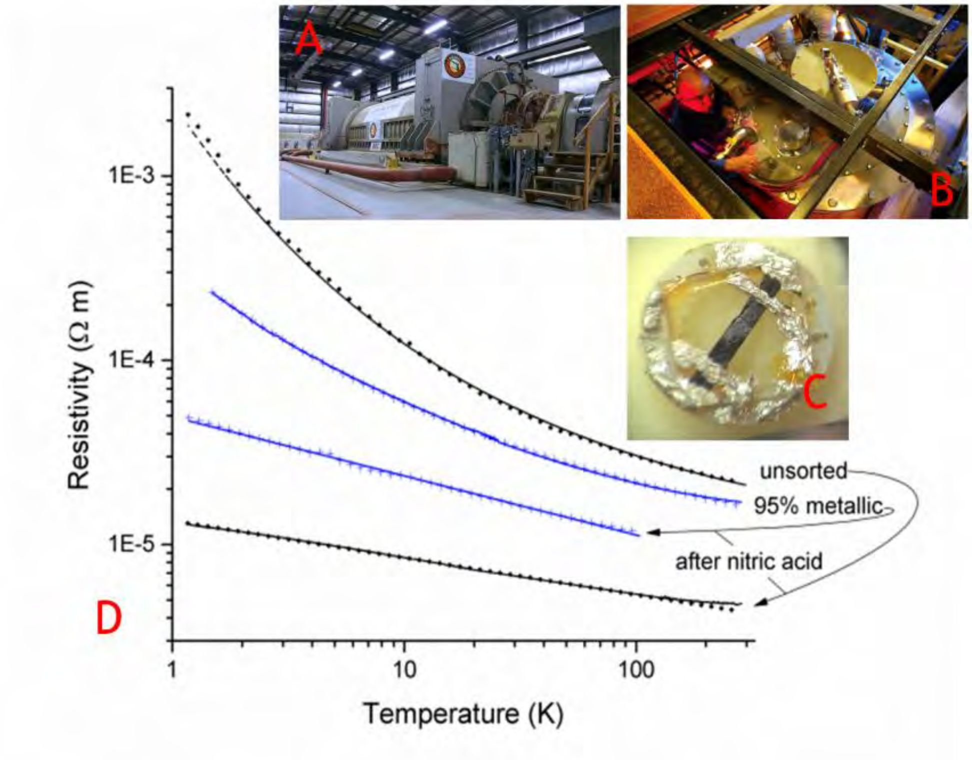


Figure 8. A. The magnet we used is powered by one of the world's largest generators pictured here. It is used as a gigantic flywheel. **B.** The cryogenic magnet capable of 100 T. In our study we only wnet to 60 T. **C**. An example of the material under test—A CNT film in the standard four probe configuration. **D.** Resistance versus temperature data for both typical unsorted nanotubes and those composed of the predominantly metallic variety, in a doped and undoped state.

Next we will show the effect on resistance of sweeping the ambient magnetic field at cryogenic temperatures. These experiments were accomplished at the High Magnetic Field Laboratory in Los Alamos, NM. We went to magnetic fields far higher (~60 T) then what is achieved in typical magnet laboratories across the world. A picture of the magnet, the sample, and the magnet's power supply is shown in the captions in figure 8. With these measurements, the metric we measure is not resistance by itself, but magnetoresistance *MR*, which is the change of resistance normalized by the original resistance: MR= (R(B)-R(0))/R(0).

In general, literature reports that CNT MR at first decreases and then increases with increasing field, and this too is what we find—at least at low field (See figure 10). What is interesting is what happens at higher field. For films consisting of randomly aligned CNT materials, we see the MR saturating at around 20 T. This is a brand new result and demonstrates that the basic MR increase brought on by the magnetic field is from a spin saturation mechanism. This finding is in contrast to models commonly used by other authors (who do not have access to these large magnets). Aligned CNT material made at Cambridge however has no indication of saturation, which is a further indication that another charge transport mechanism is at play (See figure 9). In this alternate picture, the MR increases is likely brought on by the shrinking of the electron wave function.

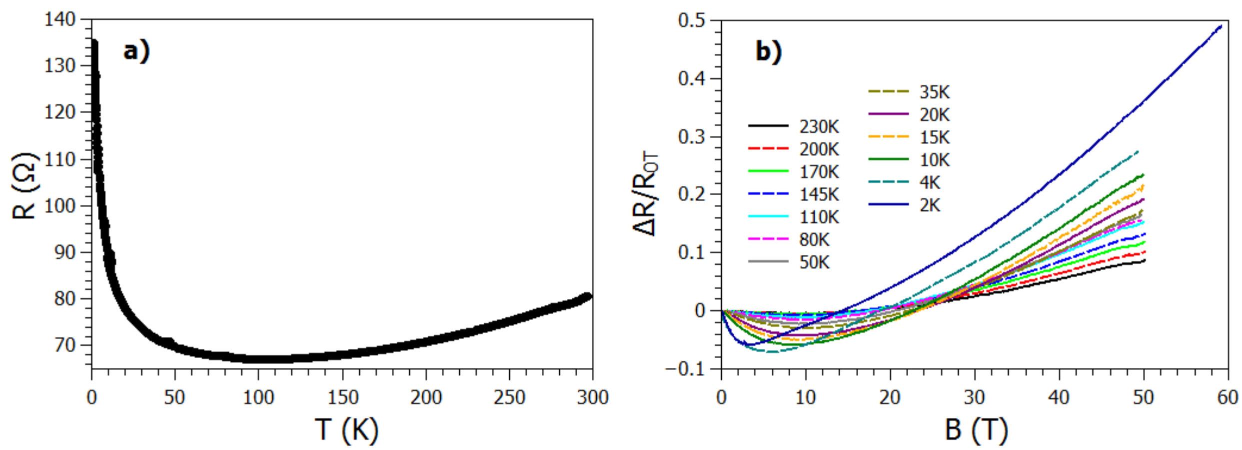


Figure 9. A| Resistance versus temperature of the highly aligned CNT material made at Cambridge and **B|** the magnetic field dependence. Unlike the randomly aligned CNTs, there is no sign of MR saturation under high magnetic field.

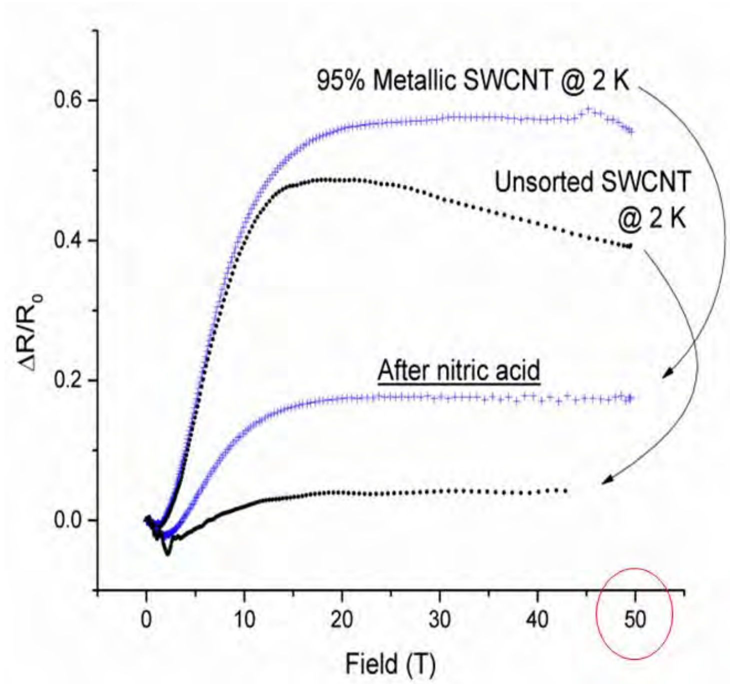


Figure 10. MR showing at first a decrease, followed by an increase and then a level off. This is for the randomly aligned CNTs.

CNT Distillation with High Power Lasers. Sweeping field, frequency, and temperature, while interesting, are for material characterization. At the end of the day, what is required is conductivity improvement. There has been some work with doping, but nothing over a threefold increase in conductivity. Following is a laser post-treatment process that increases the alignment, crystallinity, and purity of CNT assembles and leads to a dramatic increase in the electrical and thermal conductivity of the bulk material (early experiments indicate an order of magnitude increase in specific conductivity).

The CNT assembly is illuminated by a high intensity laser and, under the right conditions, all CNTs not forming a sufficiently conductive thermal pathway are removed. The remaining CNTs have a five-fold increase in crystallinity without impact on the radial breathing modes (RBM) as indicated by Raman Spectroscopy. SEM indicates significantly enhanced alignment and migration of iron catalyst to the surface. As an additional post process step, this catalyst can be easily removed by wet chemistry techniques. As a result of the decrease in density, the material becomes optically transparent, which will benefit flexible touch-screen technology and microwave applications. The essence and novelty of this concept is that it is a sorting/ distillation process that keeps highly conductive CNTs and throws away non-conductive CNTs, amorphous carbon, and residual catalyst. Immediate payoff should be with the field emission emitters, which would only require treatment in the field emission areas. The following figures highlight some of the laser treatment's features.

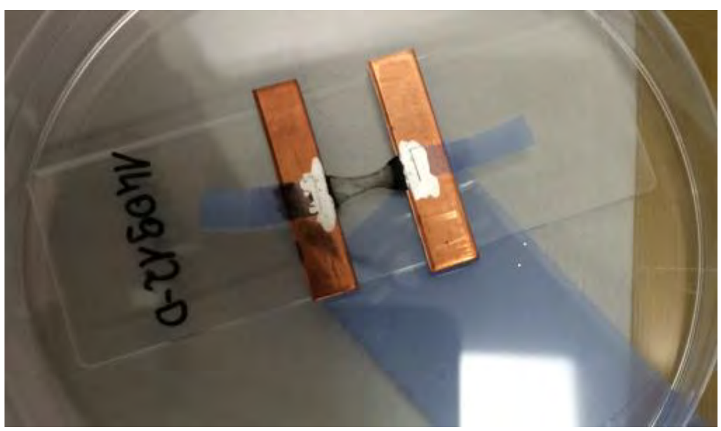


Figure 11. The laser process makes the material transparent and this is likely because it is much less dense. Provided the conductivity also improves, thin *and flexible* touch screens may me an application.

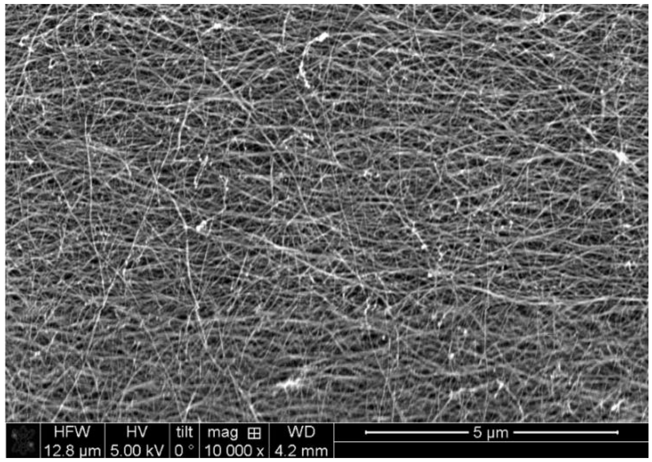


Figure 12. This is the as-is CNT material with very rough alignment going from the left to right.

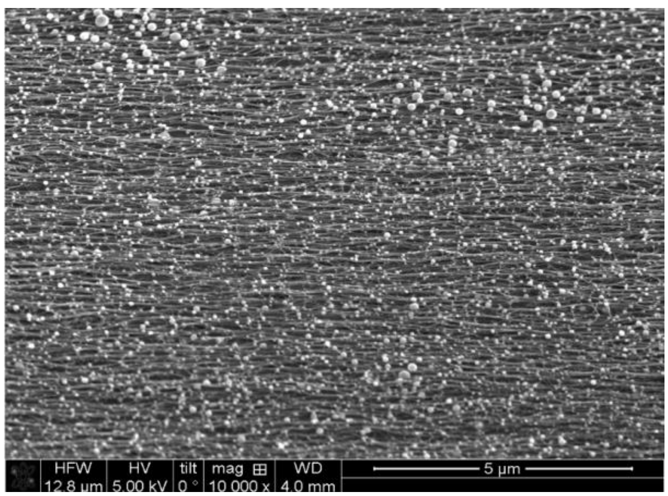


Figure 13. After the laser post step process, the material is significantly less dense and now highly aligned. Catalytic material is thrown to the outside.

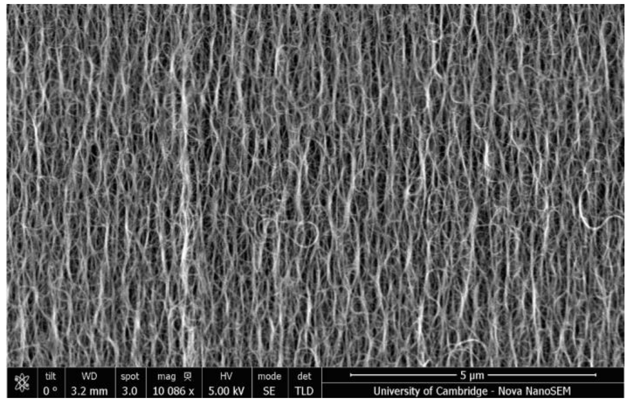


Figure 14. The catalyst may be removed with standard wet chemistry techniques and results in a ten-fold increase in the conductivity.

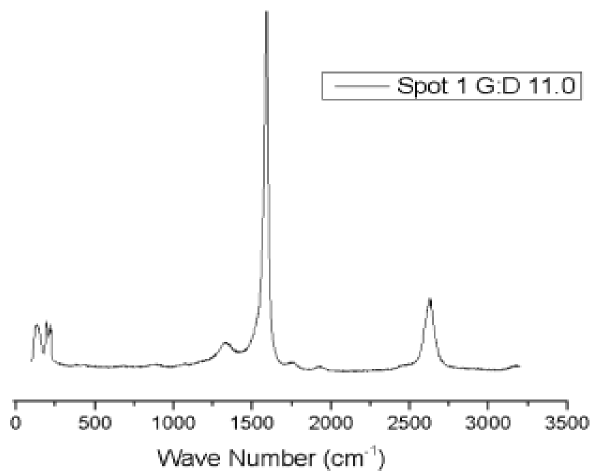


Figure 15. As-is raman spectroscopy showing a G:D ratio of 11.

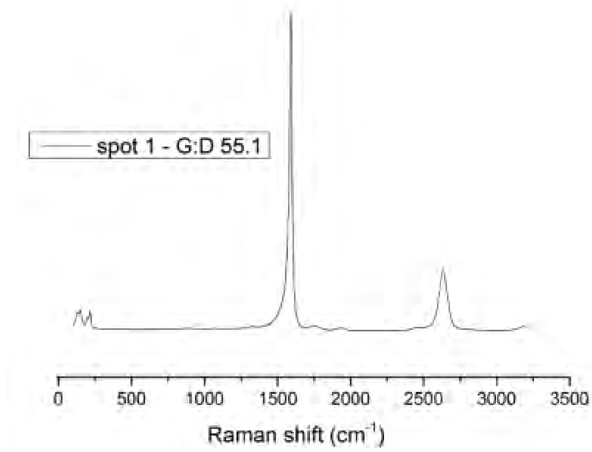


Figure 16. After laser treatment, G:D jumps five-fold and indicates a significant improvement in carbon crystallinity.

Future Work. This report was a brief summary of the work over the last three years and a lot of effort is currently underway to conclude the story. In particular, millimeter wave characterization is quite possibly very important to determine individual CNT length. CNT length is a critical parameter in electrical transport and one that is not really monitored in the floating catalyst community due to its difficulty in measuring—the traditional, laborious method being to use transmission electron microscopy to carefully scan along a 1 mm long CNT. We showed some preliminary millimeter wave results showing possibly a resonance associated with CNT length, but more measurements are underway to confirm this and millimeter wave instrumentation access is very scarce.

The laser post treatment is another effort obtaining considerable attention. We regularly achieve factor of ten improvements in specific conductivity and are around the level of gold at the moment. There is no reason to think that enhancement will end there however. The material may be further doped, condensed and annealed; work for this is aggressively underway. Magneto-resistance experiments of laser treated material like is also in progress and will hopefully show exactly why transport is so more efficient. In the interest of applications, the laser beam at the moment is about a centimeter wide. It will be difficult to scale this process as-is to treat large films. The laser process now could treat fibers as well as the small tips in CNT field emitters. Finally, a much larger lens could be ordered and expand the beam to about 5 centimeters and still keep the required intensity. This configuration would be much better suited to treat large area materials.

Papers this grant generated. As a result of this grant, several peer reviewed research papers have been published.

Fairchild, S., J. Mater. Res., Vol. 29, No. 3, Feb 14, 2014.

Cahay, M. Appl. Phys. Lett. **105**, 173107 (2014)

Bulmer, J.S. et al. Microwave Conductivity of Sorted CNT Assemblies. Sci. Rep. 4, 3762; DOI:10.1038/srep03762 (2014).

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