ORNL/TM-2022/2625
CRADA/ NFE-19-07845

CRADA Final Report: CRADA Number NFE-19-07845 with American Nanotechnologies, Inc.

Will Fitzhugh

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MANAGED BY UT-BATTELLE FOR THE US DEPARTMENT OF ENERGY

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1. Abstract

Cooperative Research and Development Agreement (CRADA) NFE-19-07845 between Oak Ridge National Laboratory (ORNL) and American Nanotechnologies, Inc. (ANI) focused on studying the use of dielectrophoresis as a mechanism to purify nanoparticles, particularly semiconducting carbon nanotubes (CNTs). The successful development of low-cost purification processes is a significant bottleneck in the adoption of semiconducting CNTs in commercial semiconducting devices. ANI is a startup company developing scalable systems for performing nanoparticle dielectrophoresis, which has previously been used only in microfluidic devices. The work done under this CRADA is exploring the use of ANI's patent resonant dielectrophoresis (r-DEP) technology and its ability to purify semiconducting CNTs at large scale. While continued work is on-going, r-DEP has proven to be a viable way to control nanoparticles in bulk dispersions. Optimization of the process is now underway to reach minimum viable product and begin material sales. Additionally, ANI and ORNL continue to collaborate on leveraging this technology to reach down the value chain and create new commercial devices.

2. Statement of Objectives

The three objectives of the CRADA, and their relevant tasks:

Objective 1: Fabricate and test high-frequency reactive-load amplifier

Description

The power requirements for ANI's r-DEP platform are not achievable using the standard off-the-shelf amplifiers that are found in conventional DEP systems. Thus, the first goal is to construct a suitable amplifier for use throughout the proposed work. ANI has completed preliminary design work on such an amplifier and has performed the requisite simulations to confirm proper operation with the intended loads.

The tasks necessary to fabricate and test the aforementioned amplifier are as follows:

1.1: Fabricate switching amplifier capable of delivering up to 100W at 0.5-4 MHz based on ANI's prior design (ANI)

1.2: Characterize performance using control resonators in the prescribed band (ANI)

1.3: Confirm system compliance with all ORNL safety standards

Objective 2: Construct resonators for targeted frequency and field intensity, establish base-line purity metrics

Description

Each dielectric phase separation of interest requires a particular frequency range and electric field intensity. For example, phase separation of metallic and semiconducting carbon nanotubes requires frequencies in excess of 1MHz and peak fields in excess of $1 kVmm^{-1}$.

Similarly, determining the purity of the processed material relies on different metrics for different materials (e.g. optical absorbance/Raman spectroscopy for carbon nanotubes). Goal 2 is to construct a resonator and establish purity base-lines that target a specific use-case material to be implemented in the full r-DEP system constructed in Goal 3.

The tasks necessary to develop the aforementioned resonators are:

2.1: Compute and/or measure critical frequency and electric field intensity ranges for inducing phase separation in the materials under test (ANI & ORNL)

2.2: Establish base-lines for the purity figures-of-merit of the material under test (ANI & ORNL)

2.3: Design resonator(s) targeting the critical field requirements of task 2.1 and optimize fluid system(s) for appropriate kinetics (ANI)

2.4: Fabricate and characterize resonator(s) (ANI)

<u>Objective 3</u>: Demonstrate prototype indicative of industrial-scale capacity

<u>Description</u>

Using the systems and base-lines resulting from Goals 1 & 2, Goal 3 aims at the demonstration of the full r-DEP system as is relevant to large-scale purification and the quantification of commercially significant parameters. Operational parameters will be optimized with respect to cost vs purity, throughput, yield, etc.

The tasks necessary to demonstrate the aforementioned prototype are:

3.1: Combine systems from Goals 1 and 2 into full r-DEP prototype (ANI)

3.2: Evaluate purity figure-of-merits under various operating condition (ANI & ORNL)

3.3: Estimate the cost for a pilot industrial-scale system (ANI)

3.4: Evaluate dielectric material(s) performance in marketable form (e.g. deposited on flexible substrate for thin-film-transistors) (ANI & ORNL)

3. <u>Benefits to the Funding DOE Office's Mission</u>

This material processing technology embodies the DOE Office of Advanced Manufacturing's mission to catalyze R&D that can drive U.S. economic competitiveness. Hugely displacive semiconducting CNT transistor applications ranging from non-volatile digital memory to 5G telecommunications to printable integrated circuits have been demonstrated using semiconducting CNTs. However, the commercial fate of these technologies' hinges on the supply of a low-cost electronics-grade semiconducting CNT source.

Compared with alternative materials, both incumbent and on the horizon, semiconducting CNTs maintain superior performance in a wide variety of transistor devices. In high performance wafer-based transistors, semiconducting CNTs' low-power consumption, high linearity and low-thermal noise make them an ideal replacement for current options (Si/GaN/GaAs/etc.). For thin-film-transistor (TFT) devices, semiconducting CNT films surpass amorphous and polycrystalline alternatives in terms of mobility and drive current, even when fabricated via simple drop-casting. This later property, the ability to fabricate suitable TFTs via printing methods rather than photolithography, is of huge economic potential. Fabrication facilities for TFT production currently cost on the order of $1-3 billion and are sensitive to quick depreciation. The compatibility of semiconducting CNTs TFTs with printing methods, particularly the ultra-low-cost roll-to-roll methods, could enable a significant reduction in the need for such costly fabs.

4. Technical Discussion of Work Performed by All Parties

Objective 1 consisted of designing, constructing, and testing a switch mode amplifier that would be compatible with the unique electrical requirements of scaled DEP experiments. In particular, the amplifier needed to be able to deliver voltages as high as 3kV to loads with parasitic capacitances as high as 50 pF at frequencies up to 4 MHz.

This was achieved by building a two-stage system. The first stage consisted of a power module that would output 50V steps with power up to 175W up to 10MHz. A Class D amplifier architecture was chosen to maximize efficiency. The block diagram for this module is depicted in Figure 1 blow. Table 1 shows typical electrical characteristics for this stage.

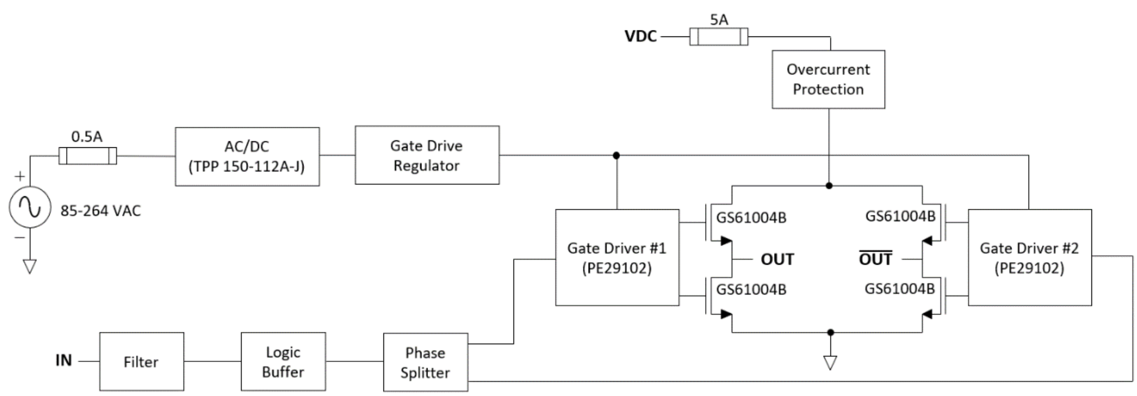

Figure 1. Block diagram for power module based on class D amplifier.

Characteristics:

DC Supply Voltage	Max	50 V
DC Current Draw	Max	3.5 A
Input Frequency	Min	160 kHz
	Max	10 MHz
Output Impedance	Typ	8 mΩ

The second-stage of this amplifier consisted of a resonant transformer with an output capacitance as high as 500 pF. An adjustable 12-500 pF variable vacuum capacitor with 10 kV, 7A rating was selected. The schematic for this stage is shown in Figure 2.

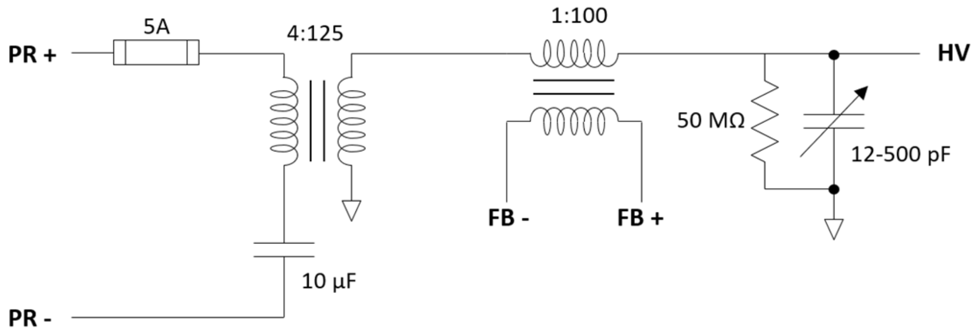

Figure 2. Resonant transformer stage with output capacitance up to 500 pF.

The final construction is shown in Figure 3.

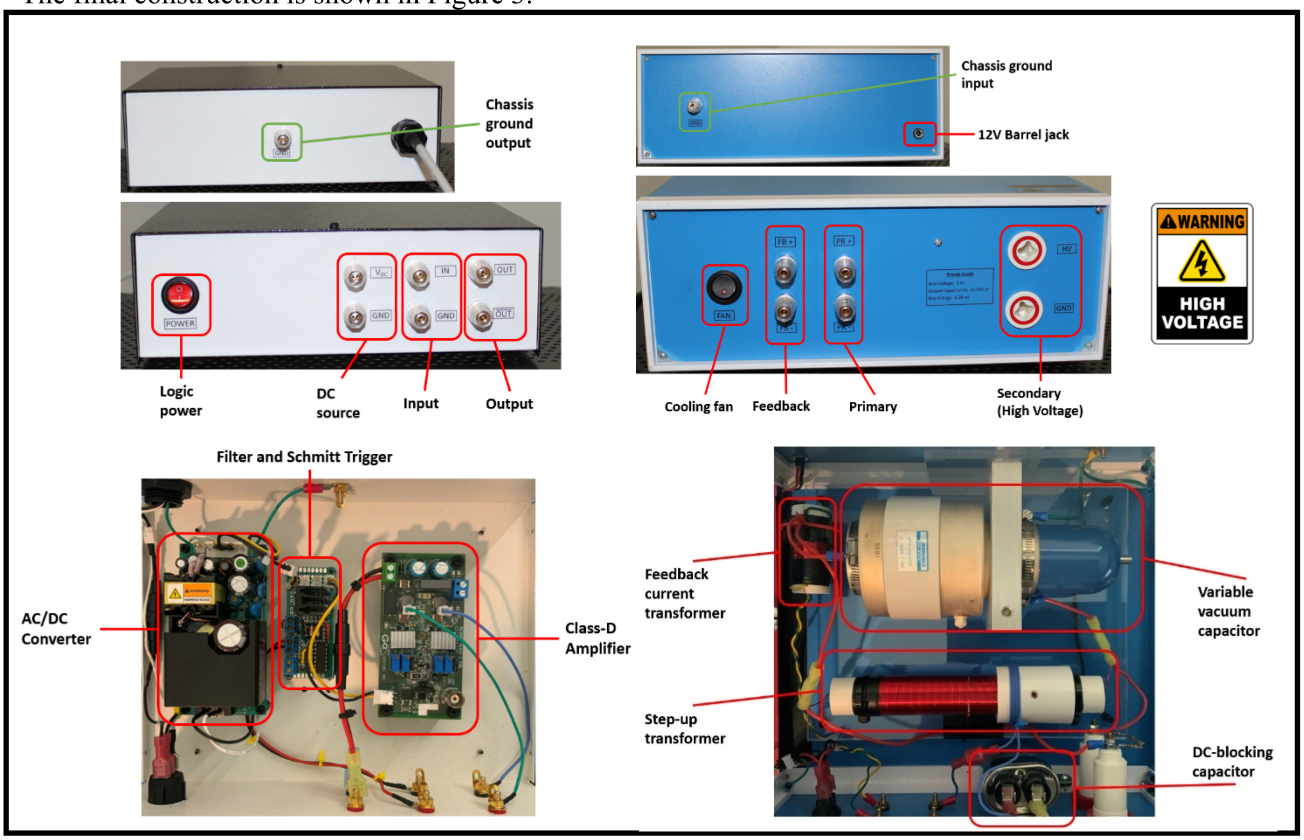

Figure 3. Power (left) and resonator (right) stages for r-DEP high-voltage amplifier.

Task 2.1 was computationally performed for a variety of carbon nanotube dimensions and dispersion conditions. Figure 4 shows the magnitude and polarity of the DEP force on a typical nanotube source and dispersion. The semiconducting CNTs (s-SWNTs) show a strong change beginning at approximately 2MHz, completely reversing polarity at approximately 20 MHz.

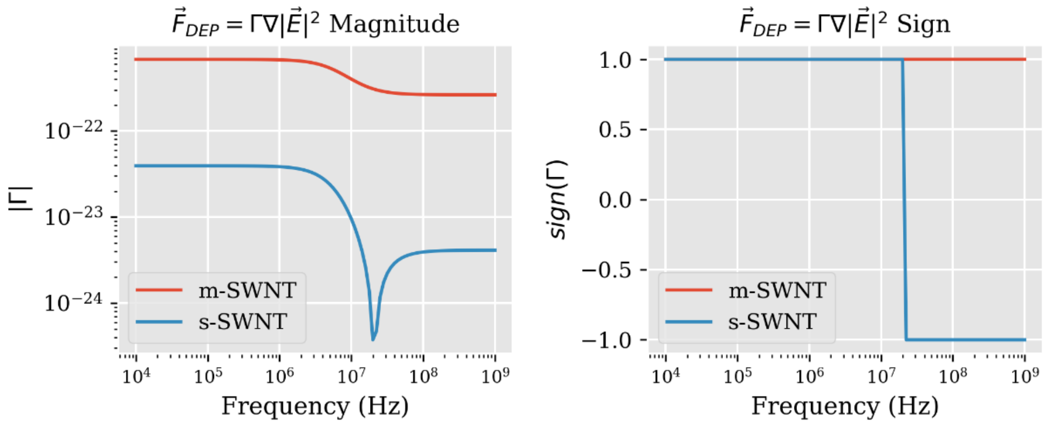

Figure 4. Magnitude (left) and polarity (right) of the DEP force on semiconducting and metallic CNTs (s/m-SWNTs). The raid change above 2MHz for s-SWNTs indicates that r-DEP should be performed above this frequency range.

Significant dendritic growth was observed at 10x lower fields than were anticipated in a CNT dispersion exposed to fields at 2MHz (Figure 5). This is believed to be analogous to the "pearl chaining" seen in traditional DEP of cells in microfluidic environment. Both the morphology and the lower electric field requirements are consistent with this view. By reducing the required voltages, this phenomenon has the added benefit of allowing us to perform r-DEP at high frequencies. To this end ANI purchased a Class A 5-50MHz amplifier. The resonators have been retrofitted for use with this new amplifier.

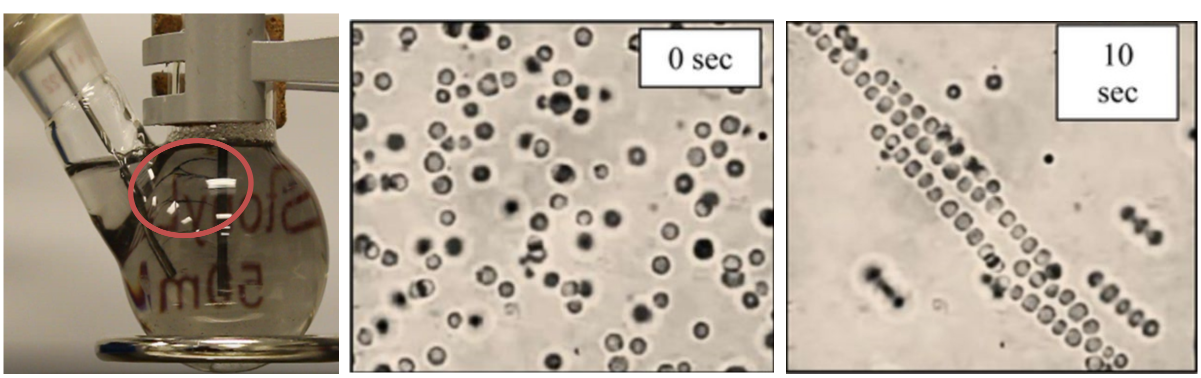

Figure 5. (left) Dendritic assembly of CNTs between two electrodes at approximately 300 V, 2 MHz. (center, right) Illustration of pearl chaining phenomena in traditional DEP. Images from Pethig, R. J. Electrochem. Soc., 164, 5 (2017), pp. B3049-B3055

Task 3.1 is on-going with adaptations being made to account for the strong dendritic growth observed at low field conditions. Such growth presents a problem for free solution processing as the dendrites quickly short the system. However, it also presents an opportunity in that these dendrites form at much lower field strengths providing an opportunity for more robust implementations. Currently, ANI is focusing on combining r-DEP with column chromatography. Column chromatography is a low-cost method for CNT purification but has the ultimate problem that, by itself, it can only reach semiconducting CNT purities on the order of 95%. ANI is currently developing a column system that performs chromatography alongside dielectrophoretic filtration via an r-DEP implementation to increase purification to the 99%+ purities needed for commercialization. This approach is showing promising results (Figure 6). ANI is currently optimizing its chromatography methods. This method is on track to provide enough materials for beachhead material sales in the near future.

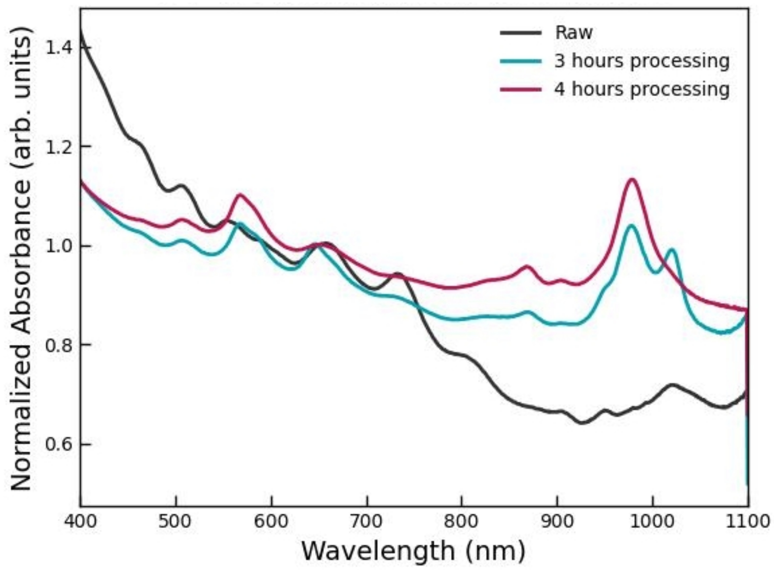

Figure 6. Absorption spectra for CNTs before and after processing show significant removal of metallic CNT content.

ANI is continuously refining its cost models for this processing technology at scale. Forecasts continue to suggest that we will be able to deliver the resulting materials at an order of magnitude lower cost that currently available methods at scale. In Task 3.4, drop-casted semiconducting CNT films for use in chemical and biochemical sensors has been identified as a high value add product. Moving into this sensor space is a major focus of continued collaboration between ANI and ORNL (section 7).

5. Subject Inventions (As defined in the CRADA)

None

6. Commercialization Possibilities

Processing costs for purifying semiconducting CNTs remains the prohibiting bottleneck for their adoption in commercial devices. Original target markets, such as thin film transistor devices and/or high-speed devices, stand to gain significantly from semiconducting CNTs. However, the entry barriers in these fields are unlikely to be overcome in the near future. ANI believes that the best balance of high-growth potential and low-barrier to entry application segments is that of chemical and biochemical detection. Unlike those prior market segments, there is no incumbent material in the space of chemical/biochemical detection. ANI has identified beachhead use-cases for the defense industry and is working on developing a corresponding go-to-market strategy for non-defense counterparts.

7. <u>Plans for Future Collaboration</u>

ANI continues to work with ORNL's Center for Nanophase Material Science (CNMS) on leveraging semiconducting CNTs for developing chemical and biochemical sensors. ANI has been awarded an NSF Phase I SBIR for demonstrating that semiconducting CNT gas sensors can be drop casted, a key manufacturing technique for low-cost devices. ANI is currently drafting a user proposal at CNMS to leverage ORNL resources as part of this effort. Similarly, ANI is applying for a Phase II STTR from the Department of the Air Force for demonstrating compatibility of r-DEP enriched CNTs with cortisol sensors which were previously developed at Air Force Research Labs. These cortisol sensors showed initial promise, but lack a scalable supply chain. This Phase II STTR will focus on showing that r-DEP can provide performance enhancing high-purity semiconducting CNTs at a cost tolerable to the Air Force for widespread adoption. Again, ANI plans to leverage resources at CNMS for this STTR work via a user proposal.

8. <u>Conclusion</u>

During this CRADA, r-DEP processing technology has been scaled to the 100-watt level. Combining r-DEP with column chromatography is proving to be a cost-effective way to obtain semiconducting CNTs at the high purity levels needed for commercialization. ANI and ORNL are continuing to reach down the value chain, leveraging this material processing technology to build new sensor devices. Follow on funding from the Department of Defense and the National Science Foundation has been obtained to develop commercial products based on this technology.