FROM BENCH TOP TO MARKET: GROWTH OF MULTI-WALLED CARBON NANOTUBES BY INJECTION CVD USING FE ORGANOMETALLICS - PRODUCTION OF A COMMERCIAL REACTOR

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Abstract

Preferential oriented multiwalled carbon nanotubes were prepared by the injection chemical vapor deposition (CVD) method using either cyclopentadienyliron dicarbonyl dimer or cyclooctatetraene iron tricarbonyl as the iron catalyst source. The catalyst precursors were dissolved in toluene as the carrier solvent for the injections. The concentration of the catalyst was found to influence both the growth (i.e., MWNT orientation) of the nanotubes, as well as the amount of iron in the deposited material. As deposited, the multiwalled carbon nanotubes contained as little as 2.8% iron by weight. The material was deposited onto tantalum foil and fused silica substrates. The nanotubes were characterized by scanning electron microscopy, transmission electron microscopy, Raman spectroscopy and thermogravimetric analysis. This synthetic route provides a simple and scalable method to deposit MWNTs with a low defect density, low metal content and a preferred orientation. Subsequently, a small start-up was founded to commercialize the deposition equipment. The contrast between the research and entrepreneurial environments will be discussed.

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From Bench Top to Market: Growth of Multi-Walled Carbon Nanotubes by Injection CVD Using Fe Organometallics - Production of a Commercial Reactor

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March 18, 2009 – Meeting-in-Miniature

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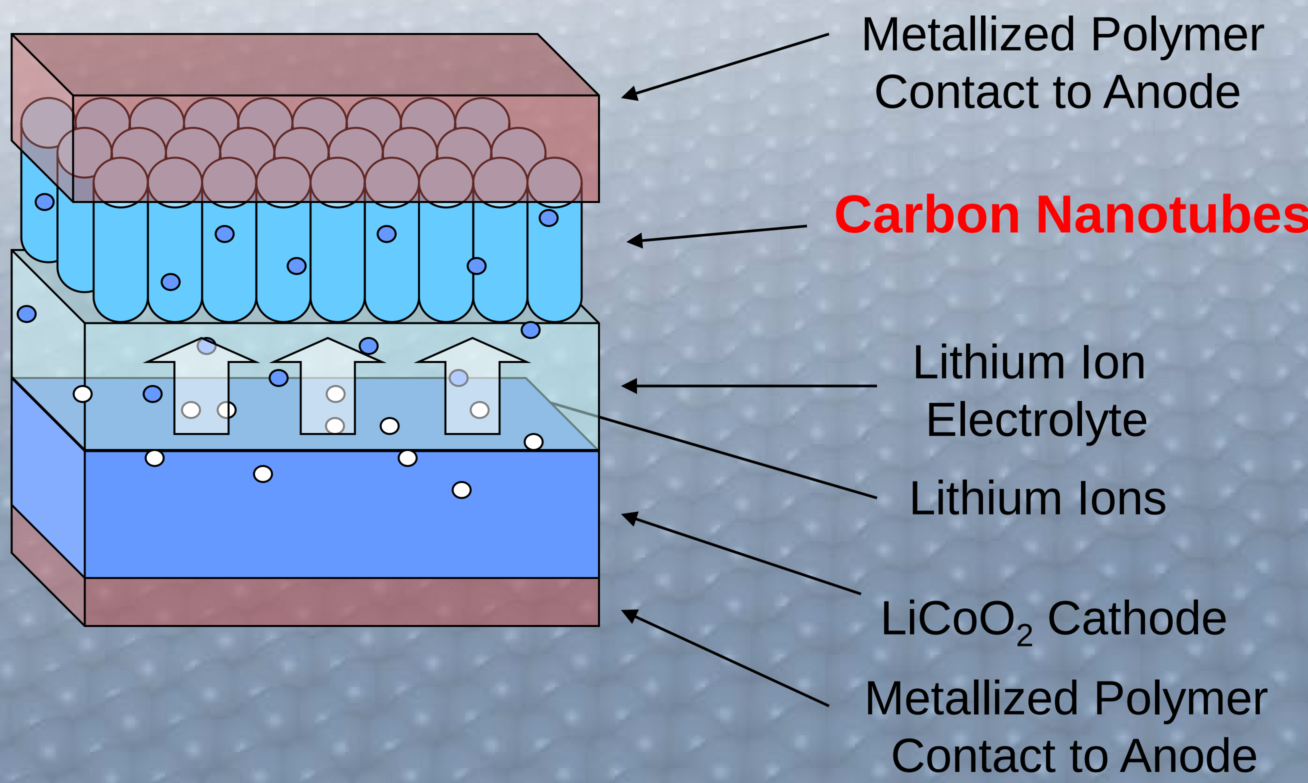
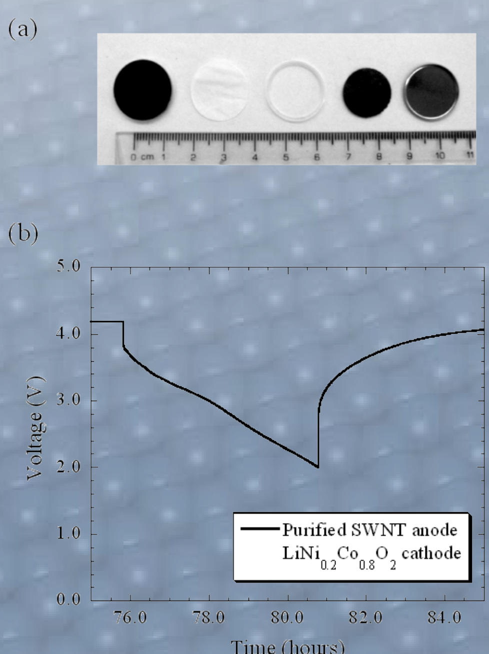
Carbon Nanotube Lithium Ion Batteries

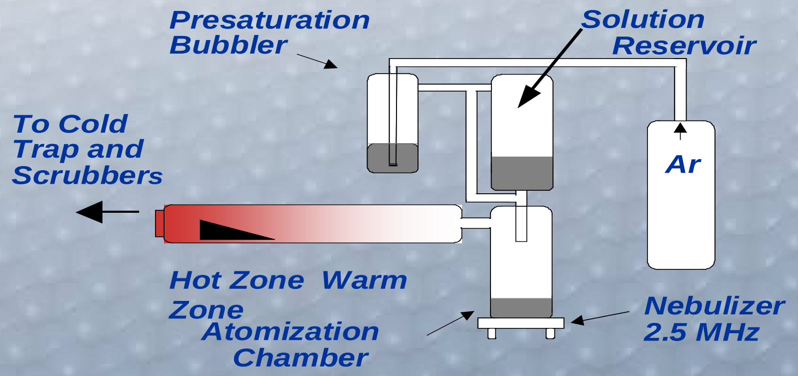
Battery is charged by driving Li ions from $LiCoO_2$ through polymer electrolyte into carbon nanotubes





Incorporation of carbon nanotubes into Li^+ batteries depicting (a) coin cell components with (b) the discharge data for a coin cell containing purified SWNT anode and $LiNi_{0.2}Co_{0.8}O_2$ cathode operating at 25 ºC.

Multi-walled Carbon Nanotubes Grown by Spray Pyrolysis

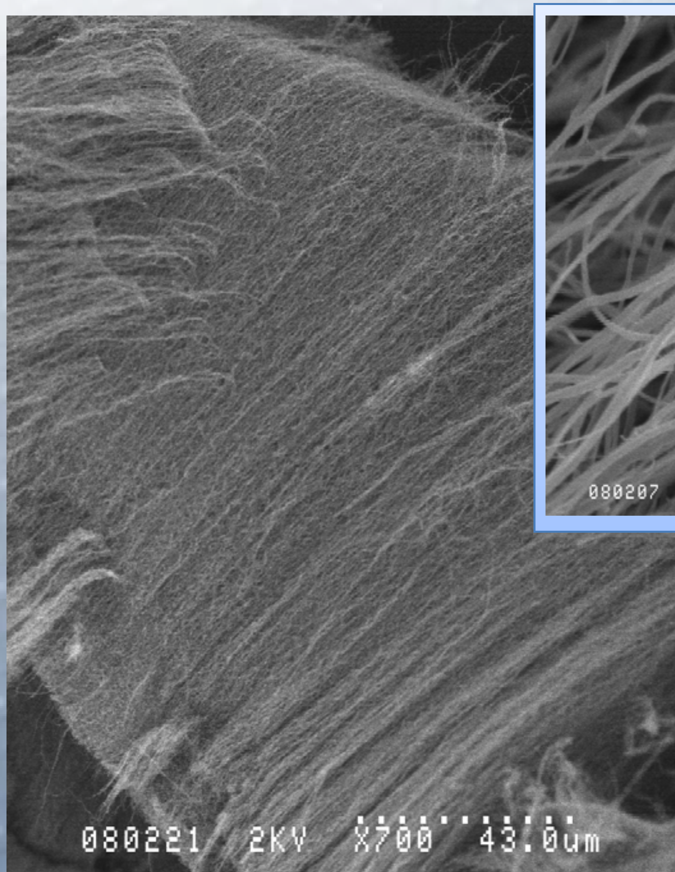


Horizontal Chemical Spray Pyrolysis or CVD Reactor

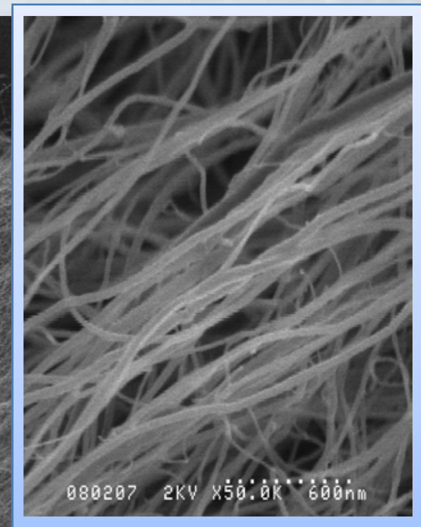
Key Features of Our Process:

- Two-zone furnace.
- Iron OM catalyst in toluene.
- Syringe pump delivery.
- H_2/N_2 or H_2/Ar carrier gas.
- Deposit at 650-800˚C.
- Deposit on SiO_2 and Ta foil.

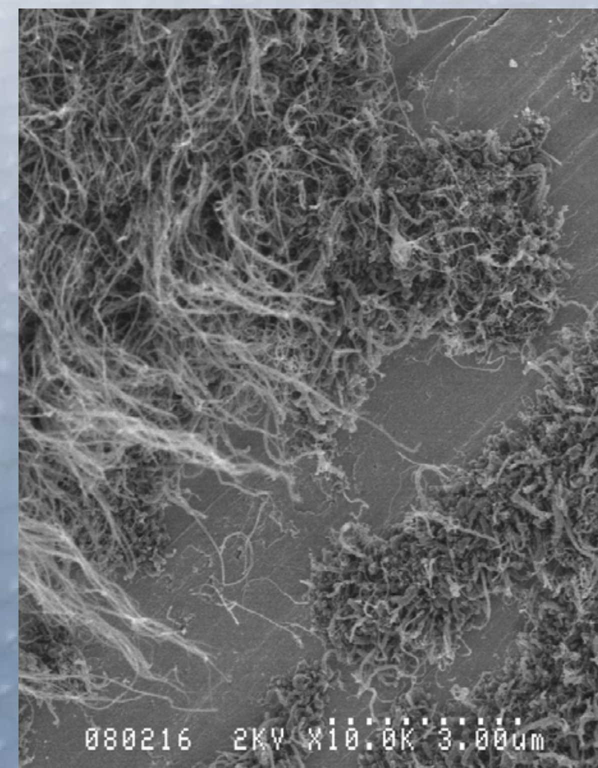
SEMs of (Aligned) Multi-walled Carbon Nanotubes*



Cross-section



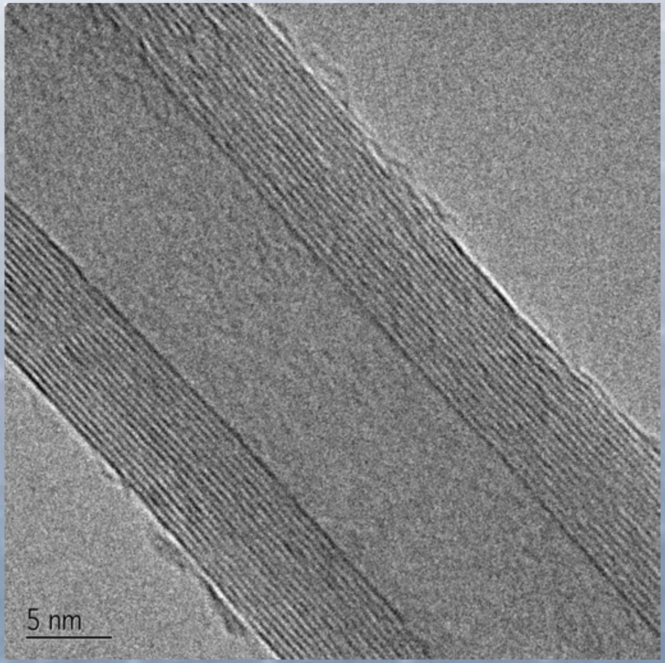
Close up



SEM image of carbon nanotubes grown on a tantalum substrate. Note incomplete surface coverage.

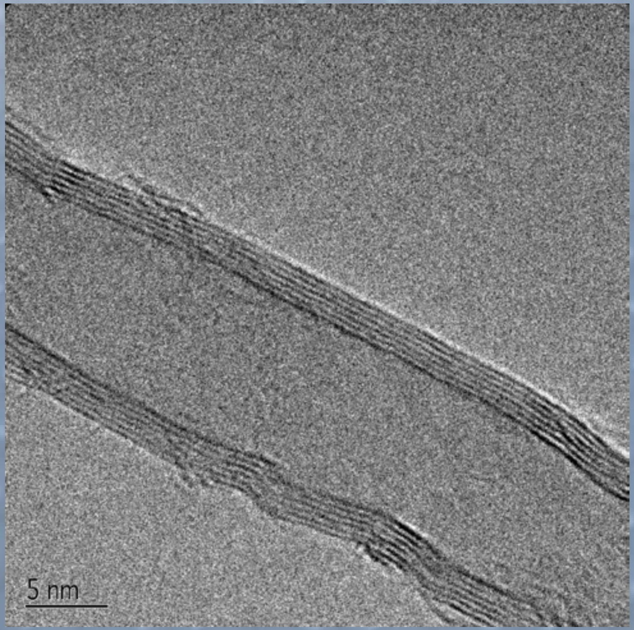
* - JD Harris‡, RP Raffaelle, T Gennett, BJ Landi, and AF Hepp‡; MSEB 116 36-374 (2005).

Characterization by TEM

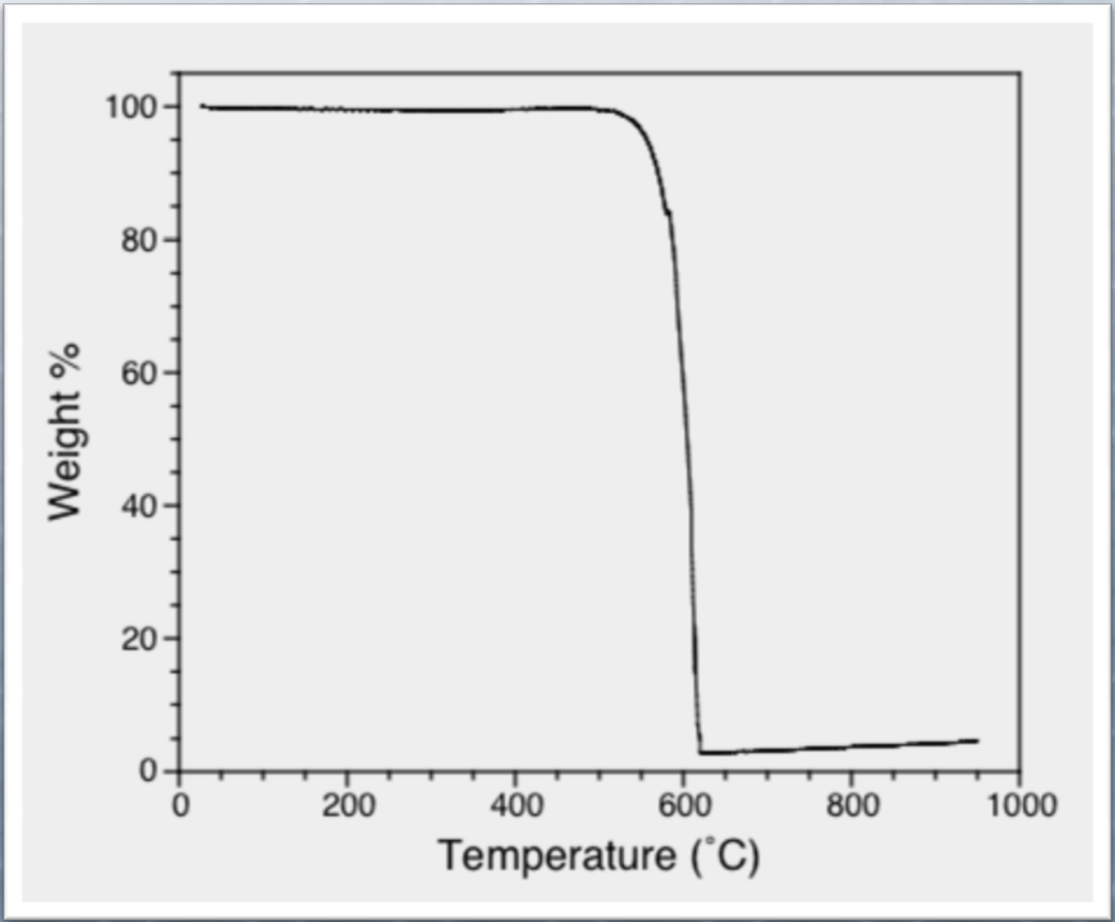


Multi-walled tubes with a large size distribution:

- 15 - 200 nm OD
- 2.6 - 32 nm ID
- Smallest tubes had 6 walls

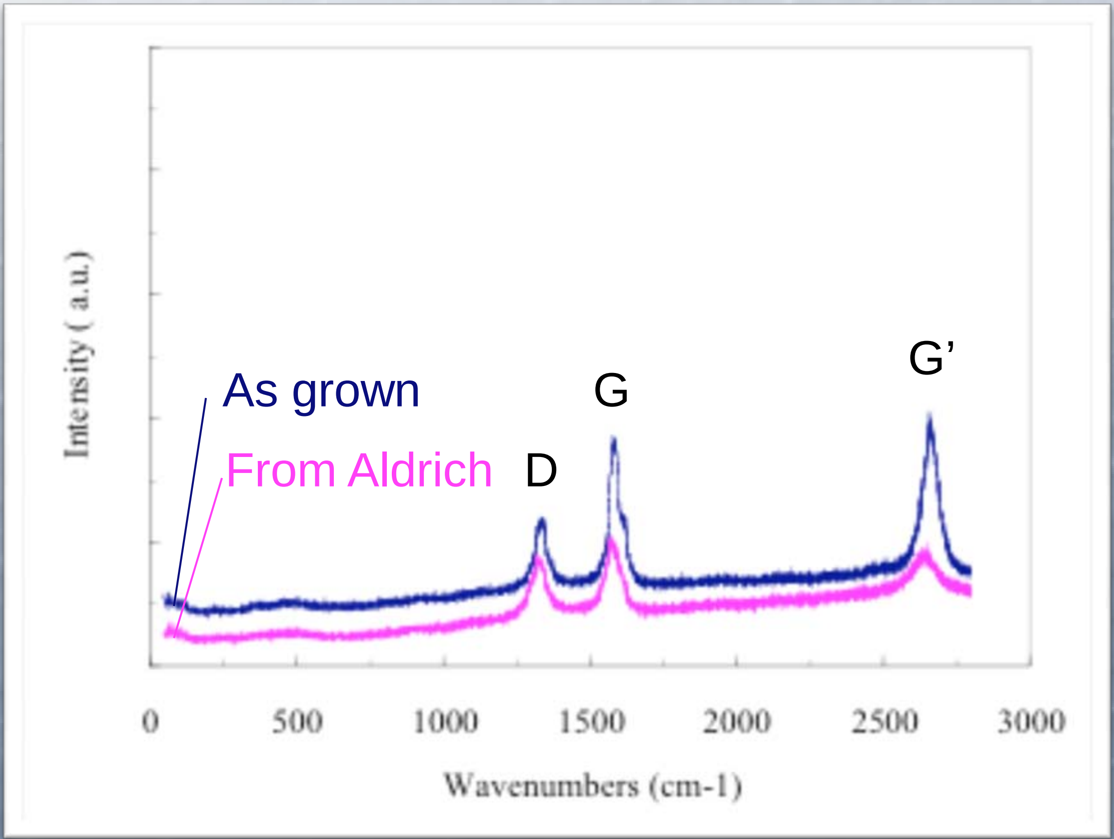


Characterization of MWC Nanotubes by TGA



- < 1% Wt. Loss by 520˚C
- Max Wt. Loss at 609˚C
- Complete C loss by 625˚C
- As grown material contains **< 3 wt. % iron**
- Others report 7 - 22 wt. % metal

Characterization of Nanotubes by Raman Spectroscopy*



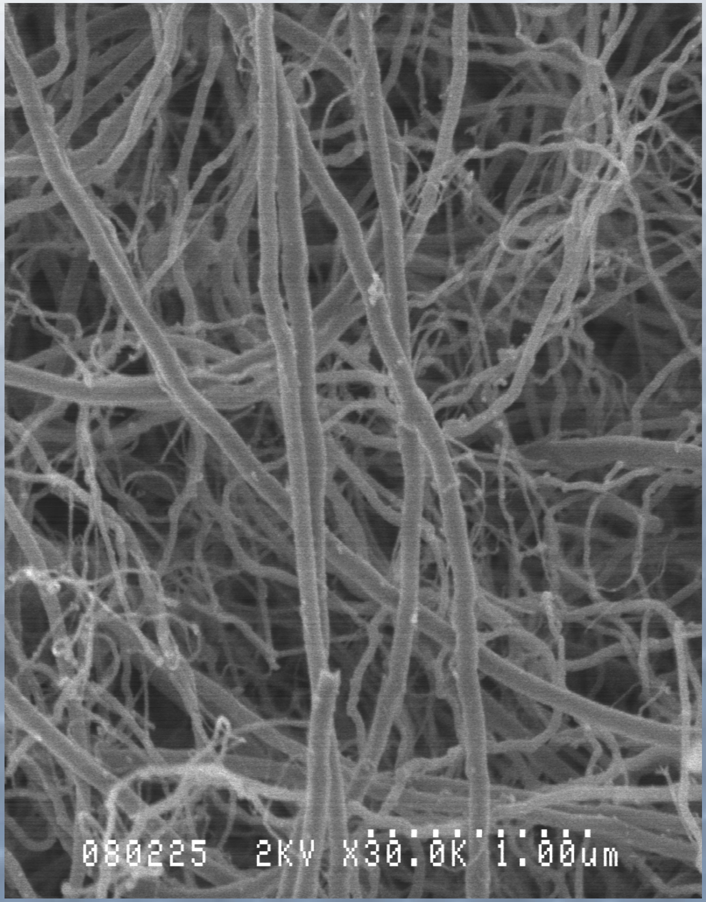
- GRC-MWNT sample (blue) MWNTs from Aldrich (pink)
- D-band is related to disorder, defects & sp^3 bonded materials
- G-band indicative of crystallinity
- G' band indicates long-range order
- Large sharp G-band is an indication of less disorder

Comparing ratio NASA G'/D to Aldrich shows GRC-MWNT are much cleaner

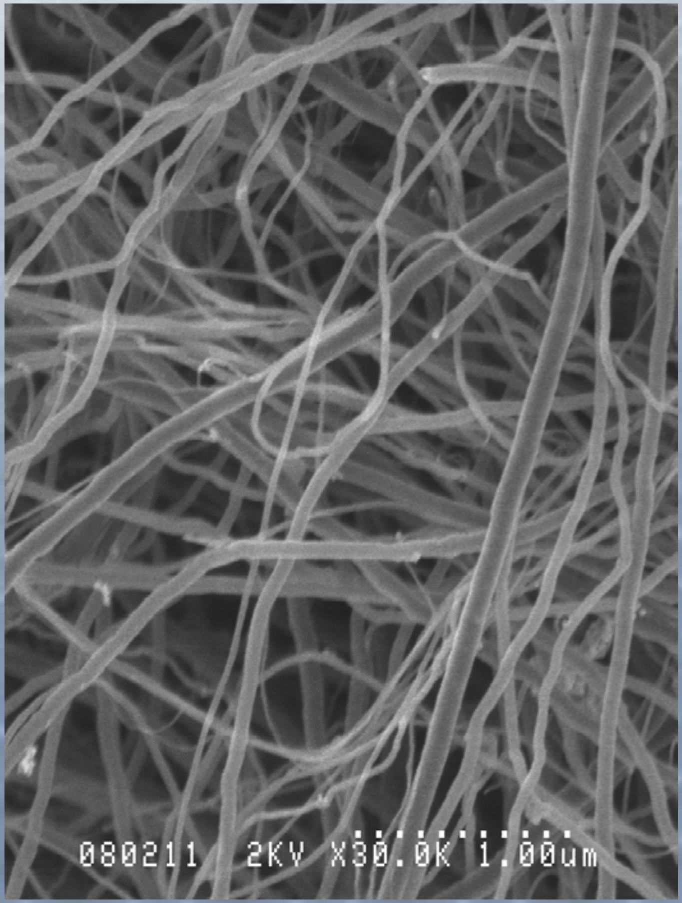
Intensity of NASA D* to Aldrich also demonstrates superior purity

* - RA Di Leo, BJ Landi, and RP Raffaelle‡; Journal of Applied Physics **101** 064307 (2007).

Heat Treatment of MWCNT



MWCNT as produced



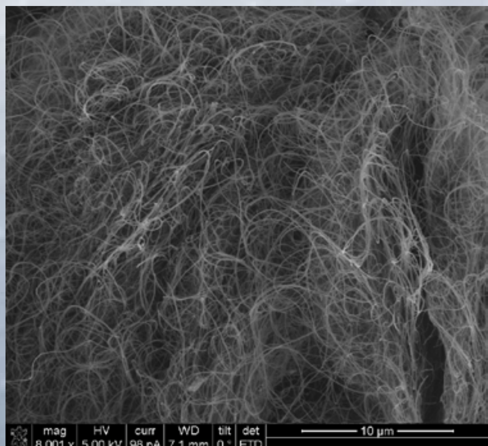
Heat treated under CO_2

Technology Transfer: NASA GRC to NTI

Harris & Hepp
NASA GRC
2003

Individual IP
Disclosures
2004-5

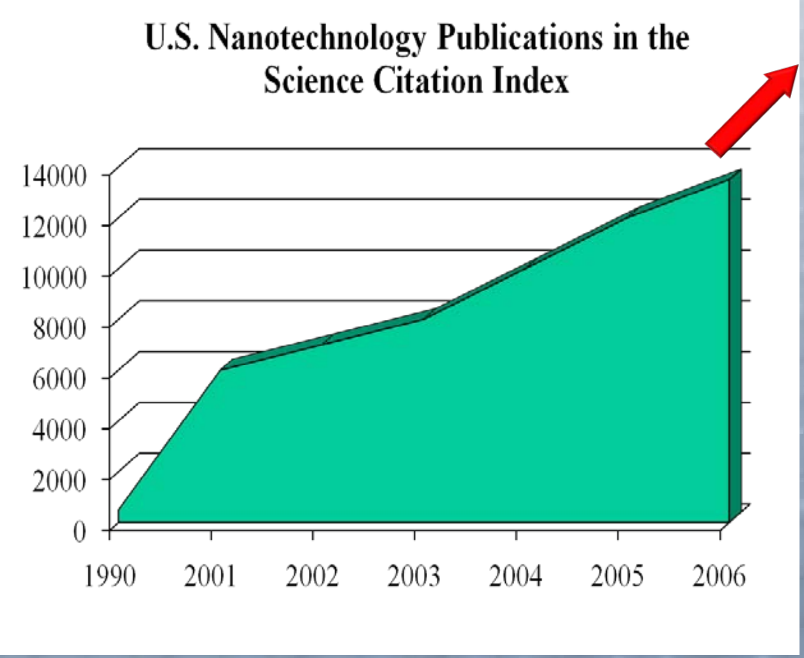
IP Migration
NASA Rights to AFH
NNU Rights to JDH
Joint Patent Application
2005-6



Technology Demonstration at NTI
Dave Scheiman and Jon Cowen

Rowsell, DM Flood,
and DJ Flood

The Explosion in Nanotech Research



But if you want to play…

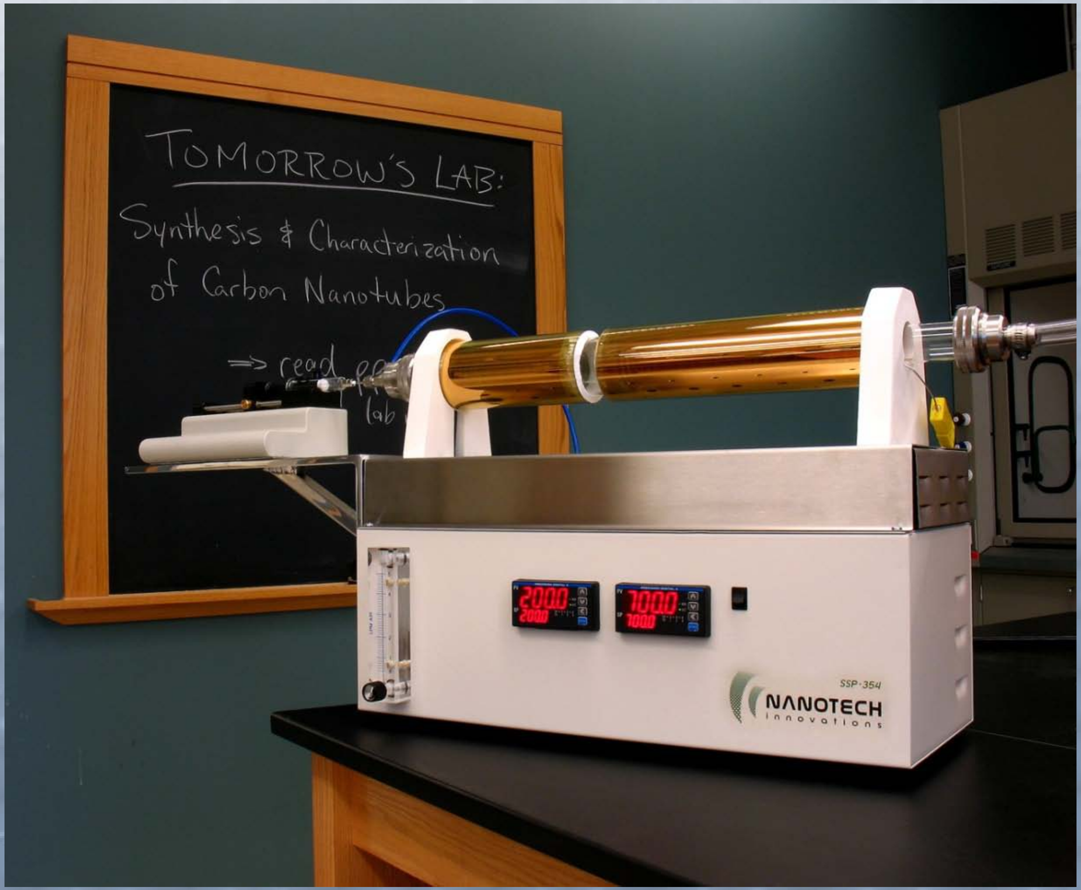
There are significant problems…

Variability in batches
Mixtures
High level of impurities
Do you get what you pay for?

Nowhere is this greater than for carbon nanotubes (CNTs)

CNT = $290 million in 2006; est. $1.9 billion 2010 (80% growth)

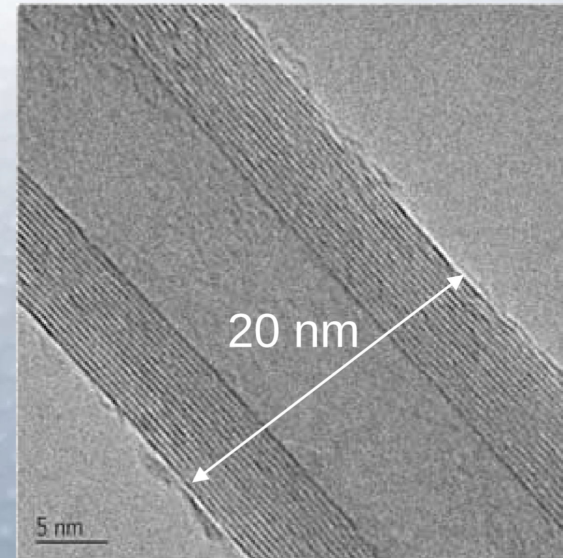
The solution to consistent CNT supply…
Nanotech Innovations SSP-354

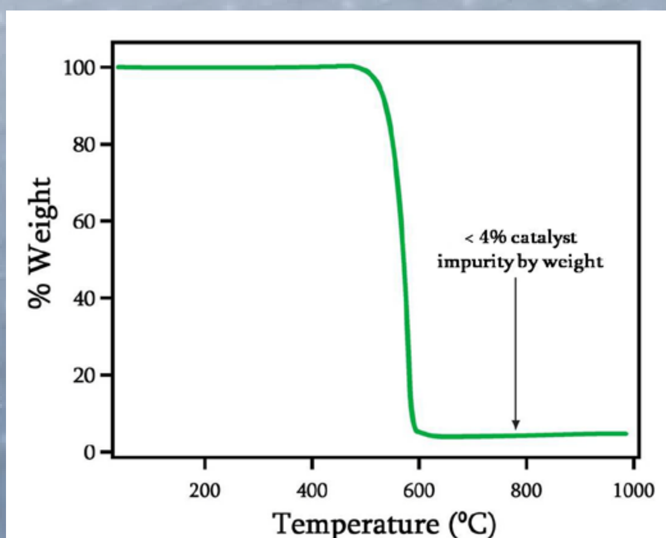


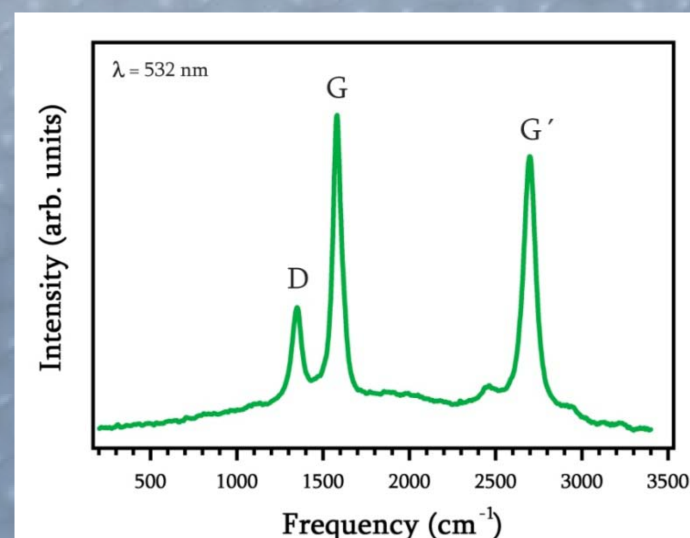
NASA Technology - Company owns IP – Patent Pending

How good are Nanotech Innovations' as-prepared CNTs?

Prepackaged catalyst/C source
Highly uniform CNTs
Low catalyst content
Low non CNT content
No purification necessary







High school student can produce 200 mg/day

Potential Market

- Educational market defines the initial scope
- U.S. Department of Education, National Center for Education Statistics show at least 4,300 post-secondary schools in the United States

U.S. Degree Granting Colleges and Universities (2006-07)

Type of School	Number
Public 4-year	643
Public 2-year	1045
Private 4-year	1986
Private 2-year	640
Total	4314

SOURCE: U.S. Department of Education, National Center for Education Statistics,
Higher Education General Information Survey (HEGIS)

- Multiple departments (Physics, Chemistry, etc)
- 1% minimum annual penetration in US ≈ 100 sales per year

Business Growth Opportunities

Small-to-large business - Just in time supply with consistent quality

Medical research - Controlled purity

Single wall nanotubes (SWNT) - Company to address this market

SWNT growth process development

Aggressive marketing and sales program

Easily doubles/triples market opportunity

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