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

J. Rowsella,‡, A.F. Heppb,‡, J.D. Harrisb,c, R.P. Raaffeled, J.C. Cowena,b, D.A. Scheimana,b, D.M. Flooda and D.J. Flooda,b

aNanotech Innovations, Inc., 132 Artino Street, Oberlin OH 44074
bNASA Glenn Research Center, Cleveland, OH 44135
cDepartment of Chemistry, Northwest Nazarene University, Nampa, ID 83686
dDept. of Physics, Rochester Institute of Technology, Rochester, NY 14623

Abstract

Preferred 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.

‡Corresponding authors:
Jesse Rowsell - Tel.: (440) 926-4888
Email: info@nanotech-innovations.com
URL: http://www.nanotech-innovations.com/index.html

Aloysius F. Hepp - Tel.: (216) 433-3835
Email: Aloysius.F.Hepp@nasa.gov
From Bench Top to Market: Growth of Multi-Walled Carbon Nanotubes by Injection CVD Using Fe Organometallics - Production of a Commercial Reactor

J. Rowsell\textsuperscript{a,†}, A.F. Hepp\textsuperscript{b,‡}, J.D. Harris\textsuperscript{b,c}, R.P. Raffaelle\textsuperscript{d}, J.E. Cowen\textsuperscript{a,b}, D.A. Scheiman\textsuperscript{a,b}, D.M. Flood\textsuperscript{a} and D.J. Flood\textsuperscript{a,b}

March 18, 2009 – Meeting-in-Miniature

\textsuperscript{a}Nanotech Innovations, Inc., 132 Artino Street, Oberlin OH 44074
\textsuperscript{b}NASA Glenn Research Center, Cleveland, OH 44135
\textsuperscript{c}Department of Chemistry, Northwest Nazarene University, Nampa, ID 83686
\textsuperscript{d}Dept. of Physics, Rochester Institute of Technology, Rochester, NY 14623
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.
- H₂/N₂ or H₂/Ar carrier gas.
- Deposit at 650-800°C.
- Deposit on SiO₂ and Ta foil.
SEM image of carbon nanotubes grown on a tantalum substrate. Note incomplete surface coverage.

* - JD Harris‡, RP Raffarelle, 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 & sp³ 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

Heat Treatment of MWCNT

MWCNT as produced

Heat treated under CO$_2$
Technology Transfer: NASA GRC to NTI

Individual IP Disclosures 2004-5

Harris & Hepp NASA GRC 2003

IP Migration
NASA Rights to AFH
NNU Rights to JDH

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


<table>
<thead>
<tr>
<th>Type of School</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Public 4-year</td>
<td>643</td>
</tr>
<tr>
<td>Public 2-year</td>
<td>1045</td>
</tr>
<tr>
<td>Private 4-year</td>
<td>1986</td>
</tr>
<tr>
<td>Private 2-year</td>
<td>640</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>4314</td>
</tr>
</tbody>
</table>


- 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
Contact info.

Nanotech Innovations
132 Artino St
Oberlin OH 44074
phone (440) 926-4888
fax (440) 926-4885

www.nanotech-innovations.com

info@nanotech-innovations.com
quotes@nanotech-innovations.com