CARBON NANOTUBE SYNTHESIS

TUTORIAL at NT06

Nagano, Japan, June 18, 2006

Prof. Dr. Esko I. Kauppinen

NanoMaterials Group

Center for New Materials and Laboratory of Physics

Helsinki University of Technology

Espoo, Finland
Collaboration

Dr. Albert G. Nasibulin (aerosol synthesis of CNTs)
Dr. Hua Jiang (HR-TEM, ED/TEM)
Dr. David P. Brown (combined aerosol-CFD modelling)
Dr. David Gonzalez (charging of CNT’s)
Dr. Paula Queipo (cluster-catalyzed surface CVD synthesis of CNTs)
Prof. Sergei D. Shandakov (Marie Curie Fellow 2006-07, high yield synthesis)
Andrei Ollikainen, Anton Anissimov (growth and applications in electronics)

Prof. Daniel E. Resasco, Oklahoma U., USA (CVD growth & chirality)
Prof. David Tomanek, Michigan State U., USA (atomic modelling)
Dr. Peter V. Pikhitsa, Odessa Nat. Univ., Ukraine (SWCNT Nucleation)
Prof. Risto Nieminen, Dr. Arkady Kraseninnikov, COMP/HUT Finland (atomic modelling)
Dr. Bernd Freitag, FEI, Netherlands (C_s-TEM imaging)

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* Academy of Finland via TULE program/ELENA Consortium
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Tutorial Material
Dr. A. Loiseau, Prof. S. Maruyama, Prof. M. Endo, Prof. S. Iijima, Prof. K. Bolton, Prof. S. Farhat, Dr. C.D. Scott, Dr. Chris Kingston
Contents

• Properties to be controlled – focus on SWNT
• Physical methods (brief)
  – Arc discharge
  – Laser methods
• CVD methods
  – Floating catalyst (detailed)
    • HiPCO
    • Hot Wire Method
    • DIPS
    • NT nucleation mechanisms based on MD simulations
    • Catalyst particle growth modelling
  – Substrate CVD methods (brief)
    • CoMoCat
    • ACCVD
    • Chirality
• Individual NTs – controlling bundling via gas-phase charging (new)
• Simultaneous Floating Catalyst CVD synthesis of fullerenes and NTs – in-situ functionalization of tubes with fullerenes – new material "Carbon Nanobud" (new)
Three allotropic modifications of carbon: diamond, graphite, and fullerene structures (fullerenes and CNTs).
Carbon Fiber/Nanotube Products

- Single Walled Carbon Nanotube
- Multi-walled Carbon Nanotube (CNT)
- Carbon Nanofiber
- VGCF’s
- Carbon Fibers

Electrical, Mechanical, Thermal Properties

Tube Diameter, nm

Options:
- 1
- $10^1$
- $10^2$
- $10^3$
- $10^4$
Prof. Endo VGCNF
SEM images of vapor grown carbon nanofibres produced by Showa Denko, Fine Carbon Department, Nagano, Japan, by floating catalyst CVD method
(courtesy Dr. Hua Jiang)
Known forms of Carbon Nanomaterials

**Carbon Nanotube (SWCNT):**
Roll of carbon sheet one atomic layer thick
*1 000 000 times thinner than paper*

Rolling in different directions makes different kinds of tubes

- *(10,10)* armchair tube
  - METALLIC
- *(10,5)* helical (chiral) tube
  - SEMICONDUCTING

Courtesy Prof. S. Maruyama
Chirality Map

Zig-zag; (n,0) ; chiral angle = 0

Armchair = All metallic

Others metallic only when (m – n) = n*3, n= integer

Semiconducting when (m - n) ≠ n *3
Distance from origin is proportional to nanotube diameter.
Properties to be controlled during synthesis

- Number of walls (SW, DW, MW)
- Diameter
- Length, orientation
- Purity (catalyst and non-tubular carbon)
- Bundling
- Chirality
- Functionalization
Physical methods

- **Arc discharge**

High electrical current is applied between two carbon electrodes. Carbon plasma is generated from anode (positive), forms nanotubes and deposits on cathode (negative).
GAS PHASE GROWTH OF CATHODE DEPOSIT

ELECTRIC-ARC DISCHARGE

History

WISKERS 1960


FULLERENE 1985


FULLERENES 1990


MWCNT 1991


SWCNT 1993


Courtesy Prof. S. Farhat
TEM images of commercial SWCNTs produced (2002) by arc-discharge – no purification
(courtesy Dr. Hua Jiang)
SWCNT PARAMETERS


- Gas type: Helium
- Pressure: \( P = 660 \text{ mbar} \)
- Voltage: \( V = 40 \text{ V} \)
- Current: \( I = 100 \text{ A} \)
- CATALYSTS: \( \text{C:Ni:Y} \ 94.8:4.2:1 \text{ atom \%} \)
- ACD: \( d = 1 \text{ mm} \)

- Erosion rate: \( V_{\text{soot}} = 5-20 \text{ mg/s} \)
- CNT contents: 10-40 Weight \% (70 % for Journet et al.)
SWCNT YIELD vs ARC CURRENT

TEM images of commercial SWCNTs produced by arc-discharge – no purification. Fullerenes on tubes

courtesy Dr. Hua Jiang
Laser vaporization

Graphite target is shot by laser, as a result carbon is vaporized and forms carbon nanotubes.
TEM images of commercial (2002) laser oven produced SWCNTs- no purification

courtesy Dr. Hua Jiang
“Double-Pulse” YAG Method

\( \sim 1 \text{ g/day @ 60-90\%} \)

- 1200°C
- Ar: 100 sccm, 500 torr
- 523 nm (490 mJ) and 1064 nm (550 mJ)
- 42 ns delay
- 2“ and 1“ quartz tubes

\( \sim 10 \text{ g/day @ 40-50\%} \)

- 1100°C
- Ar: 750 sccm, 500 torr
- 2 x 1064 nm lasers (930 mJ)
- 40 ns delay
- 4“ quartz tube only


Courtesy Chris Kingston NRC Canada
CO$_2$-Powder Method

• cw CO$_2$ 2.1 kW
• 2 l/min Ar/N$_2$
• 3 g/hr powder
• CoNi (2.5 at-% each)
• 1100°C

500 mg in 10 minutes at ~20-40 %


Courtesy Chris Kingston NRC Canada
Pulsed + CW Method

Laser #1: Vaporization
• 1064 nm, 30 Hz, **1.6 J/pulse**

Laser #2: Excitation
• 1064 nm, CW, **50 W**


Courtesy Chris Kingston NRC Canada
Raman Shift (cm$^{-1}$)

- 100
- 200
- 300
- 1200
- 1300
- 1400
- 1500
- 1600

Intensity (arb.)

- Two Lasers (CW+Pulsed)
- Single Laser (Pulsed)

G/D = 21
G/D = 426

$\lambda = 514$ nm

>400 mg/hr
~70 % SWNT

- CW Laser provides more efficient vaporization and modifies thermal gradients

Temperature (°C)

- 0
- 100
- 200
- 300
- 400
- 500
- 600
- 700
- 800
- 900

Differential Mass (mg/°C)

- -0.8
- -0.6
- -0.4
- -0.2
- 0.0
- 0.2
- 0.4
- 0.6
- 0.8

Relative Mass (%)

- 0
- 20
- 40
- 60
- 80
- 100

TGA

- 50°C

Courtesy Chris Kingston NRC Canada
Investigations of single-wall carbon nanotube growth by time-restricted laser vaporization
(2002)

Alex A. Puretzky,1,2 Henrik Schittenhelm,1 Xudong Fan,1* Michael J. Lance,1 Larry F. Allard Jr.,1 and David B. Geohegan1

Summary of the results from the in situ imaging and spectroscopic diagnostic investigations of SWNT's growth inside a hot oven. Actual images of the laser plasma (t<200 µs) and Rayleigh-scattering images of the plume (t>200 µs) are shown vs time (scale in cm at right). During the first 100 µs after ablation, the laser plasma is very hot, and emission from excited atoms and molecules dominate LIF from ground-state species. Ground-state populations then peak and subsequently disappear due to condensation.
Continuous CNT synthesis laser reactor (Loiseau et al.)

**CW CO₂ laser vaporization**

**Conditions:**
- target C:Co:Ni (98:2:2 at. %);
- helium 50 ml/s, 300 hPa;
- constant target surface temperature Ts: (3200-3500 K)

• Gavillet et al. in JNN 2004, 4, 346.  
  Courtesy A. Loiseau
Laser-based techniques

- **Coherent Anti Stokes Raman Scattering (CARS)**
- **local thermometry, T**

- **Laser Induced Incandescence (LII)**
  - imaging carbonaceous aggregates and soot and volume fraction measurement (number density, sizes)

- **Laser Induced Fluorescence (LIF)**
  - Diagnostic of atoms and small molecules
  - Ni, Co, Fe, C₂, C₃


Courtesy A. Loiseau
HiPCO: Gas-phase (floating catalyst CVD) method for SWNT production

Fe(CO)$_5$ decomposition in high-pressure CO
HiPco Mixing Zone

Optical Pyrometer to measure temperature

Cooled Fe(CO)$_5$ in CO

Water-cooled Injector

Copper Nozzle

Hot CO

SWNT Creation Zone

Single-piece Graphite Showerhead

Courtesy R. Hauge
Commercial SWCNT’s made with traditional Floating Catalyst Method (HiPCO method, CNI)

courtesy Dr. Hua Jiang
A novel floating catalyst method for SWCNT synthesis


Physical Production (PVD) of Catalyst Clusters via Vapor Nucleation-Condensation using Hot Wire Generator (HWG)
Schematic presentation of experimental setup

Catalytic reactions:

$$\text{Fe} \quad \text{CO} + \text{CO} = \text{C}(s) + \text{CO}_2$$

$$\text{Fe} \quad \text{H}_2 + \text{CO} = \text{C}(s) + \text{H}_2\text{O}$$
Lab reactors

Reactor 1

Reactor 2

Reactor 3 (behind Reactor 2)
Early results -50 nm long SWNT’s (1200 °C)

\[ \frac{D_{\text{part}}}{D_{\text{CNT}}} = 1.6 \]


CO flow rate of \( Q_{\text{CO}} = 400 \text{ cm}^3/\text{min} \)

Temperature, °C

Diameter, nm

Carbon nanotubes

Catalyst particles

10.00 nm
X300000

0.40 µm
X7300
TEM images of longer SWCNT’s at 924 °C with stainless steel rector tube using CO as carbon source and H₂/N₂ mixture through the Fe catalysts cluster source.

Growth at 575 °C
When & where SWCNT's nucleate - *in situ* sampling.

\[ Q_{tot} = 800 \text{ scm}^3/\text{min} \]
\[ \Rightarrow 3150 \text{ cm}^3/\text{min (at 900 ° C)}. \]

\[ L = 1.5 \text{ cm (894 - 908 ° C)} \]

Centerline sampling:

**Residence time**: \( \tau = 0.054 \text{ s.} \)

**CNT length** \( l = 60 \text{ nm} \).

\[ \Rightarrow \text{CNT growth rate exceeds} \ 1.1 \mu \text{m/s} \]
Comparison of FT-IR spectra obtained at the conditions of CNT synthesis at 924 °C and after switching HGW off - stainless steel reactor tube

Conditions of CNT synthesis: CO – 50 %, CO₂ – 100 ppm, H₂O – 38 ppm, CH₄ – less than 2 ppm, HCN - 20 ppm and 2 ppm (HWG on and off)

Clean Ceramic Reactor Tube: NO NANOTUBES - ONLY CARBON COATED Fe CLUSTERS
Reactor wall conditions important due to the synthesis of small amount of H₂O and CO₂ at SS (or catalyst covered) reactor surfaces!
Similarly, adding oxidant to aid SWNT forest growth:
* water - Hata et al.
* oxygen – Dai et al.
* alcohol – Maruyama et al., Windler et al. etc.

\[
\begin{align*}
CO + CO & \rightleftharpoons C(s) + CO_2 \\
H_2 + CO & \rightleftharpoons C(s) + H_2O
\end{align*}
\]
Effect of experimental conditions on the CNT length - CNTs are 60 nm long in CO+H$_2$/N$_2$ with 2 s average residence time

<table>
<thead>
<tr>
<th>Additives</th>
<th>Concentration</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>1000 ppm</td>
<td>no effect on length</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0, 150, 330 ppm</td>
<td>up to 300 nm long</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1000 ppm (clean reactor)</td>
<td>length up to 200 nm</td>
</tr>
<tr>
<td>H$_2$</td>
<td>50 %</td>
<td>up to 500 nm</td>
</tr>
</tbody>
</table>
CNT Monitoring with DMA

Carbon nanotubes

Catalytic reactions:

\[
\begin{align*}
\text{Fe} & \quad \text{CO} + \text{CO} = \text{C}(s) + \text{CO}_2 \\
\text{Fe} & \quad \text{H}_2 + \text{CO} = \text{C}(s) + \text{H}_2\text{O}
\end{align*}
\]
Monitoring SWCNT production via number size distributions of the aerosol product measured by DMA after the reactor (stainless steel tube).

Real-Time Monitoring of CNT Formation:
DIFFERENTIAL ELECTRICAL MOBILITY ANALYSER (DMA)

Potential difference (V) → Mobility (cm²/Vs) → Particle size (nm)
Correlation between diameter of Fe particles and SWCNTs — controll of CNT and Catalyst size

D\textsubscript{part}/D\textsubscript{CNT} = 1.6

Diameter of catalyst particles

Diameter of CNTs

CO flow rate of $Q_{\text{CO}} = 400 \text{ cm}^3/\text{min}$

Temperature, °C

Diameter, nm

Carbon nanotubes

Catalyst particles

$Q(H_2/N_2) = 400 \text{ cm}^3/\text{min}$

$Q(CO), t_{\text{furn}}, \{D\}, \sigma$

<table>
<thead>
<tr>
<th>Q(CO), cm$^3/min$</th>
<th>$t_{\text{furn}}, °C$</th>
<th>D, nm</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>1000</td>
<td>1.35</td>
<td>1.36</td>
</tr>
<tr>
<td>400</td>
<td>1200</td>
<td>1.76</td>
<td>1.26</td>
</tr>
<tr>
<td>590</td>
<td>1200</td>
<td>1.84</td>
<td>1.23</td>
</tr>
<tr>
<td>765</td>
<td>1200</td>
<td>1.75</td>
<td>1.22</td>
</tr>
<tr>
<td>400</td>
<td>1400</td>
<td>2.06</td>
<td>1.27</td>
</tr>
</tbody>
</table>

$Q(CO), t_{\text{furn}}, \{D\}, \sigma$

<table>
<thead>
<tr>
<th>Q(CO), cm$^3/min$</th>
<th>$t_{\text{furn}}, °C$</th>
<th>D, nm</th>
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<tr>
<td>400</td>
<td>1000</td>
<td>0.84</td>
<td>1.24</td>
</tr>
<tr>
<td>400</td>
<td>1200</td>
<td>1.12</td>
<td>1.28</td>
</tr>
<tr>
<td>590</td>
<td>1200</td>
<td>1.17</td>
<td>1.21</td>
</tr>
<tr>
<td>765</td>
<td>1200</td>
<td>1.15</td>
<td>1.19</td>
</tr>
<tr>
<td>400</td>
<td>1400</td>
<td>1.27</td>
<td>1.40</td>
</tr>
</tbody>
</table>
The $D_{\text{catalyst}}/D_{\text{CNT}}$ ratio is constant at higher growth rates?

**YES**

Number distributions of CNT diameters and lengths and catalyst particle diameters for different concentrations of H$_2$ at 924 °C.
## Ratio between diameters of catalyst particles and CNTs

Pre-made Fe particles introduced in conditions of CNT formation

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Ratio</th>
<th>$H_2$ concentration</th>
<th>$D_{CNT}$, nm</th>
<th>$D_{Fe}$, nm</th>
<th>$D_{part}/D_{CNT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{furn}$, °C</td>
<td>$Q_{CO}$, cm$^3$/min</td>
<td>$D_{part}/D_{CNT}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>400</td>
<td>1.60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>400</td>
<td>1.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>590</td>
<td>1.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>765</td>
<td>1.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1400</td>
<td>400</td>
<td>1.62</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>1.07</td>
<td>1.4</td>
<td>2.1</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1.3</td>
<td>2.1</td>
<td>1.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>1.3</td>
<td>2.0</td>
<td>1.54</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Ethanol, $t_{furn}$ = 1200 °C:**

$D_{CNT} = 1.7$ nm, $D_{Fe} = 2.4$.

$D_{part}/D_{CNT} = 1.41$

---

In-situ CVD Synthesis of Particles:

Ferrocene vapor decomposition in CO at 1150 °C

$D_{CNT} = 1.3$ nm, $D_{part} = 3.1$ nm

$D_{part}/D_{CNT} = 2.4$

More details later.

HiPco CNTs


$D_{CNT} = 0.7-1.4$ nm, $D_{part} = 5-10$ nm

$D_{part}/D_{CNT} > 3$
The schematic of the CNT growth geometry

(Nasibulin, Pikhitsa, Jiang, Kauppinen, “Correlation between catalyst particle and single-walled carbon nanotube diameters”, *Carbon* 43(11), 2251-2257).

\[
2R / 2r = 1 / \cos(\theta) = 1 / \sqrt{1 - (H / 6)^2}
\]

\[
\beta = \pi - \theta
\]
Examples of pentagon and heptagon defects

Schematic presentation of CNT topology: walls consist of hexagons (6); to close the tube six pentagons (5) are needed; to make negative curvature (to join a CNT and a particle) a number of heptagons (7) is required.

Fig. 10. Model of a nanotube kink junction, with 5- and 7-rings; the tube segment at the top can be metallic whereas the bottom segment is semiconducting [32].
The schematic of the CNT growth geometry

\[ H = \text{number of heptagons at the root of CNT}, \]
\[ P = \text{number of pentagons}. \]

\[ 2R / 2r = 1 / \cos(\theta) = 1 / \sqrt{1 - (H / 6)^2} \]

\[ \beta = \pi - \theta \]

<table>
<thead>
<tr>
<th>H</th>
<th>( \frac{D_{\text{cat}}}{D_{\text{CNT}}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>1.014</td>
</tr>
<tr>
<td>2</td>
<td>1.061</td>
</tr>
<tr>
<td>3</td>
<td>1.155</td>
</tr>
<tr>
<td>4</td>
<td>1.342</td>
</tr>
<tr>
<td>5</td>
<td>1.809</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
</tr>
</tbody>
</table>
Estimating the limiting stage in the CNT formation process

1. **Volume diffusion** of a carbon atom in a-Fe crystalline phase:
   \[ D_v = D_o \cdot \exp\left(-\frac{E_{av}}{k_B T}\right), \quad D_o = 7.9 \cdot 10^{-7} \text{ m}^2/\text{s}; \quad E_{av} = 0.79 \text{ eV}. \]

2. **Diffusion** of carbon atoms on the iron surface:
   \[ D_s = a_o^2 \nu \cdot \exp\left(-\frac{E_{as}}{k_B T}\right), \quad a_o \approx 0.29 \text{ nm}, \quad \nu \approx 3 \cdot 10^{13} \text{ Hz}; \quad E_{as} = 0.35 \text{ eV}. \]

3. **Diffusion** of carbon atoms on the CNT surface:
   Characteristic time:
   \[ \tau = \lambda^2/(4D). \]

4. Process of **heptagon transformation**
   \[ \tau = \nu^{-1} \cdot \exp\left(E_{ai}/k_B T\right), \]
   where \( E_{ai} = 2.8 \text{ eV} \) was found semiempirically

5. **Nucleation** of CNTs occurs in a nanosecond time scale
   (Maruyama et al. and Ding et al.)
Characteristic times of surface and volume diffusions and carbon insertion into CNT. Kinetic data of CO disproportionation on the surface of iron particles.
Schematic presentation of heptagon transformation (CNT growth)
Schematic presentation of mechanism of CNT formation


- **End of CNT growth**
  - CO disproportionation and CO hydrogenation reactions are prohibited \((t > 900 \, ^\circ C)\)
  - Reactions of carbon release and etching:
    \[ 2CO \leftrightarrow C + CO_2 \quad \text{and} \quad H_2 + CO \leftrightarrow C + H_2O \]

- **400 °C**
  - Carbon release on reactor walls:
    \[ 2CO + C = C + CO_2 \quad \text{and} \quad H_2 + CO = C + H_2O \]
  - CO_2 and H_2O release

- **700 °C**
  - Reactions on reactor walls:
    \[ 2CO + C = C + CO_2 \quad \text{and} \quad H_2 + CO = C + H_2O \]
  - C incorporation into graphene layer
  - Reactions of carbon release and etching:
    \[ 2CO \leftrightarrow C + CO_2 \quad \text{and} \quad H_2 + CO \leftrightarrow C + H_2O \]

- **894 °C**
  - Steady-state growth of CNT
    - C incorporation into graphene layer
    - Heptagon formation
    - Reactions of carbon release and etching:
      \[ 2CO \leftrightarrow C + CO_2 \quad \text{and} \quad H_2 + CO \leftrightarrow C + H_2O \]

- **908 °C**
  - Formation of graphene layer
    - Hexagon and pentagon formation
    - CNT nucleation
    - Heptagon formation
    - C incorporation into graphene layer
    - Reactions of carbon release and etching:
      \[ 2CO \leftrightarrow C + CO_2 \quad \text{and} \quad H_2 + CO \leftrightarrow C + H_2O \]

- **400 °C**
  - Particle saturation by C
    - Reactions:
      \[ 2CO + C + CO_2 \quad \text{and} \quad H_2 + CO = C + H_2O \]
    - C release on surface
    - C dissolution

**Fe particle formation**
- Vapor nucleation
- Condensation
- Cluster coagulation
Floating Catalyst Methods for CNT Synthesis

a) HWG-based CVD of CO

b) Ferrozene-based CVD of CO
Raman (A) and In-situ sampling (B) – Ferrozone-based CVD of CO
Size Distribution changes with Time at Fixed Reactor Conditions – e.g. Fe(Cp)$_2$ & CO at 1150 ºC - similar for Fe from HWG & CO – Due to CO$_2$ formation at the reactor wall
Cs-corrected TEM images of active catalyst clusters growing SWCNTs

Sample: **Ferrozene Reactor**
1000°C with CO + H₂O
Collected to TEM grid via ESP filter

Microscope: **FEI Titan™ 80-300**
High tension (HV): 300kV

Non-active catalysts are large, covered with 1-2 graphene layer

Courtesy Dr. Bernd Freitag
Cs-corrected TEM images of Non-active large Catalyst particles coated with graphene layer

Microscope: FEI Titan™ 80-300
High tension (HV): 80 kV

Carbon atoms

Large Non-active Catalyst Particles

Sample: Ferrozene Reactor
1000 C with CO + H₂O
Collected to TEM grid via ESP filter

Courtesy Dr. Bernd Freitag
Cs-corrected TEM images of active catalyst clusters growing SWCNTs

Sample: **Ferrozene Reactor**
1000°C with CO + H₂O
Collected to TEM grid via ESP filter

Microscope: **FEI Titan™ 80-300**
High tension (HV): **300 kV**

**Catalyst is larger than the tube**

*Courtesy Dr. Bernd Freitag*
Cs-corrected TEM images of active catalyst clusters growing SWCNTs

Sample: Ferrozen
1000°C with CO + H₂O
Collected on TEM grid via ESP filter

Microscope: FEI Titan™ 80-300
High tension (HV): 80 kV

Catalyst is larger than the tube

Courtesy Dr. Bernd Freitag
Sample: **Ferrozene Reactor**
1000°C with CO + H₂O
Collected to TEM grid via ESP filter

Microscope: **FEI Titan™ 80-300**
High tension (HV): 80 kV

Catalyst is larger than the tube

*Courtesy Dr. Bernd Freitag*
Schematic presentation of SWCNT formation mechanism during ferrozene decomposition in CO
Moisala et al., CES 2006

Ferrozene decomposition slow – overlapp between CNT nucleation & growth and Ferrozene decomposition – CVD growth of catalysts
Catalysts are injected into the furnace directly through the spray nozzle.

Another Interesting Floating Catalyst Method - Direct-Injection-Pyrolytic-Synthesis (DIPS)


Supramolecular Catalysts

Catalysts are injected into the furnace directly through the spray nozzle.

Courtesy Prof. S. Iijima
Set Up for the Diameter Control

**Experimental Variables**
- Temperature 800 – 1200°C
- \( \text{C}_2\text{H}_4 \) flow rate 0 – 350 sccm

**Fixed Constants**
- Carrier Gas \( \text{H}_2 \)
- \( \text{H}_2 \) flow rate 7.0 L/min
- feed rate 64 µL/min
- Catalyst Ferrocene or Supramolecular cat.
- Promoter Thiophene

*Courtesy Prof. S. Iijima*
Diameter Control Mechanism

- **Size of Catalyst particles**
  - 1 nm
  - 2 nm
  - 5-10 nm

- **Decomposition of Toluene**
- **Decomposition of \( C_2H_4 \)**

- **Diameter Distribution of SWCNTs**
  - 0 nm
  - 1 nm
  - 2 nm
  - 3 nm
  - 4 nm

- **Flow Direction**

- **Shift of the distribution**

*Courtesy Prof. S.Iijima*
Diameter Distribution by TEM Observation

Ethylene flow 35 sccm
$2.04 \pm 0.38 \text{ nm}$

Ethylene flow 70 sccm
$1.17 \pm 0.48 \text{ nm}$

Ethylene flow 100 sccm
$0.95 \pm 0.17 \text{ nm}$
High Purity SWCNTs by DIPS Method

A sample of diameter 1.7-1.9nm for Peapods

G/D ratio > 200
CNT Synthesis - Modeling at Different Length and Time Scales

Atomic Level Simulation of Carbon Atom Transport and Ordering in Catalyst Particle and CNT Nucleation and Growth

Chemical Kinetics Modeling of Carbon Precursor Molecule Decomposition, Free Carbon Production and Etching on Catalyst Particle

Catalyst Metal Atoms

System Level Computational Fluid Dynamics and Aerosol Dynamics Modeling of Catalyst Particle Formation, Reactor Heat and Mass Transfer, Gas and Surface Chemistry and CNT Initiation, Growth and Bundling

Synthesis Reactor:

Log(#)
Log(Size)
Log(#)
Log(Size)
Log(#)
Log(Size)
Log(#)
Log(Size)
Log(#)
Log(Size)
Log(#)
Log(Size)
Log(#)
Log(Size)
Dynamics simulation of metal cluster catalyzed SWNT nucleation: a review

Kim Bolton, Feng Ding, Arne Rosén
Göteborg University
University College of Borås
Sweden
Melting Temperature of Fe Cluster vs Size

$N^{-1/3}$ dependence is also predicted by classical theories of nanocluster melting points.
Fe$_{50}$ (1 nm), 900 K, 1 C atom per 40 ps

Number of Carbon Atoms Dissolved in Fe$_{50}$ Cluster vs. Time (ns)

- a. 0 ns
- b. 1.5 ns
- c. 2.0 ns
- d. 2.5 ns
- e. 3 ns
- f. 10 ns
- g. 18 ns

Graph showing the number of carbon atoms dissolving in Fe$_{50}$ over time.
SWNT growth on ‘solid’ particles

$\text{Fe}_{300} (\text{Mpt} = 1100 \text{ K}), \text{Temp} = 1000 \text{ K}$
Route of C diffusion from addition on the surface to the SWNT end

Fe$_{300}$ (Mpt = 1100 K)
Liquid versus solid particles

Fe$_{300}$ (Mpt = 1100K)
Summary by Bolton et al.
Molecular Dynamics Simulation for Mechanism

500 Carbon & Ni$_{108}$ : 2500K

Macroscopic modelling of catalyst particle dynamics important, as (based on exp. evidence) catalyst size during NT nucleation determines NT diameter

- Catalyst nucleation (physical or chemical)
- Growth by metal vapor condensation (and via surface reaction of precursor molecules)
- Growth by collisions (coagulation and coalescence)
- Losses to reactor walls by diffusion and thermophoresis
- Fluid flow fields needs to be modelled simultaneously
- Example: Fe catalyst particle growth via collisions in HWG floating catalyst reactor (pre-made catalyst particles)
Catalyst Particle Dynamics

- General Dynamic Equation (GDE) for the time rate of change of catalyst cluster number concentration

\[
\frac{Dn}{Dt} + \frac{\partial (Gn)}{\partial v} - I_{nuc} (v^*) \delta (v - v^*) - I_{rxn}
\]

\[
= \frac{1}{2} \int_0^\nu \beta (v - \tilde{v}, \tilde{v}) n(v - \tilde{v}, t)n(v, t)d\tilde{v} - n(v, t)\int_0^\infty \beta (v - \tilde{v}, \tilde{v}) n(v, \tilde{v})n(\tilde{v}, t)d\tilde{v}
\]

- Change in number concentration with respect to time and space
- Rate of change in number concentration due to condensation/evaporation

\[
I_{nuc} (v^*) \delta (v - v^*) = \text{Rate of nucleation of new particles of critical volume } v^*
\]

\[
I_{rxn} = \text{Rate of formation of new particles due to chemical reaction}
\]

\[
\frac{1}{2} \int_0^\nu \beta (v - \tilde{v}, \tilde{v}) n(v - \tilde{v}, t)n(v, t)d\tilde{v} - n(v, t)\int_0^\infty \beta (v - \tilde{v}, \tilde{v}) n(v, \tilde{v})n(\tilde{v}, t)d\tilde{v}
\]

- Rate of change of number concentration due to coagulation
Assumptions and Boundary Conditions for 1.78 nm Premade Catalyst Particles

- **Inflow boundary conditions**
  - 50% mixture of CO and N\textsubscript{2} gases with 7% mole fraction of H\textsubscript{2} gas through inner tube
  - 400 cm\textsuperscript{3}/s inner and outer flows at 298 K
  - 1e14, 1e16 and 1e18 particles/m\textsuperscript{3} with a GSD of 1.26 and mean diameter of 1.78 nm

- **Wall boundary conditions**
  - Temperature linearly interpolated from measurements, 1200 °C set wall temperature
  - Saturated with iron vapor

- **Outflow boundary conditions**
  - Atmospheric pressure

Brown, Nasibulin, Kauppinen (2006)
CFD Calculations of Gas Conditions

Contours of Gas Temperature (C)
- \( T_{\text{furnace}} = 1200 \, \text{C} \)
- CO Flow Rate = 400 cm\(^3\)/min
- \( N_2 \) Flow Rate = 400 cm\(^3\)/min
- H\(_2\) Mole Fraction = 0.07

Velocity Vectors Colored by Axial Velocity (m/s)
- \( T_{\text{furnace}} = 1200 \, \text{C} \)
- CO Flow Rate = 400 cm\(^3\)/min
- \( N_2 \) Flow Rate = 400 cm\(^3\)/min
- H\(_2\) Mole Fraction = 0.07
Combined CFD - Particle Dynamics Assuming 1.78 nm Premade Catalyst Particles - Mean Particle Diameter - Catalyst Growth when High Concentration

Centerline Particle Mean Diameter and Gas Temperature

High conc – too large catalysts
Particle Dynamics Assuming 1.78 nm Premade Catalysts- Std. Dev. of PSD

Centerline
Std. Dev. of Particle Size Dist.
and Gas Temperature

Contour plots showing standard deviation of PSD (ND) at different locations.

- Contours of Standard Deviation of PSD (ND)
  - $M_{0,\infty} = 1 \times 10^{14} \text{#/m}^3$
  - $T_{\text{furnace}} = 1200 \degree C$
  - CO Flow Rate = 400 cm$^3$/min
  - $N_2$ Flow Rate = 400 cm$^3$/min
  - $H_2$ Mole Fraction = 0.07
  - Unsaturated Walls, Inlet Mass Fraction Fe = 1e-20

High conc – broad catalyst distr.

Coagulation Effects  Evaporation Effects
<table>
<thead>
<tr>
<th>1 Catalyst</th>
<th>2 Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition metals: Fe, Co, Ni… or their mixtures</td>
<td>Silica, alumina, zeolite…</td>
</tr>
<tr>
<td>- Ability to decompose gaseous C-containing molecules</td>
<td>- Strong metal-substrate interactions: reduce diffusion and prevent metal species for aggregating and forming unwanted large clusters</td>
</tr>
<tr>
<td>- Correlation between the SWNT Ø and the catalyst particle size</td>
<td>- Stabilisation of particles size distribution; catalyst cluster dynamics important</td>
</tr>
<tr>
<td>- Normally prepared by wet chemical routes or by depositing thin metal film on substrates by sputtering or evaporation</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3 Carbon source</th>
<th>4 Operational conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO, EtOH, CH₄,… SWNTs synthesis</td>
<td>T (600-1200 °C)</td>
</tr>
<tr>
<td>Acetylene, benzene,…precursors for MWNTs</td>
<td>feed rate, t…</td>
</tr>
<tr>
<td>Oxidazing trace gases</td>
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</tr>
</tbody>
</table>

![Diagram of CVD method](image)
Preparation of discrete Catalytic nanoparticles of various sizes

Discrete catalytic iron oxide nanoparticles with tunable diameters using an iron storage protein: ferritin

Growth of isolated SWNTs by CVD (900 °C, CH₄, 5 min) method with diameters controlled by the sizes of the catalytic particles:

3 nm CNTs from nanoparticles of 3.7 nm and 1.5 nm CNTs from 1.9 nm nanoparticles

Base-growth model: particle remains anchored on the substrate
The nanotube diameter increases as the reaction temperature increases.
Prof. D. Resasco:
Common Features of Selective Catalysts:

- Co-Mo/supports (SiO$_2$, MgO, Al$_2$O$_3$)
- Co/MCM-41
- Co-Re alloys

Starting catalyst
Catalyst Decomposition
Nucleation and Growth

Courtesy – Prof. D. Resasco
Spectrofluorimetric analysis of SWNT (Left) and HiPCO™ (Right) samples. The comparison reflects the much narrower distribution of diameter and chirality (Weisman and Bachilo).

Comparison of Diameter Distribution
CoMoCAT Vs. HiPCO
Photo-luminescence SEMICONDUCTING
TYBES ONLY

Karlsruhe U.
(Manfred Kappes et al.)

Comparison of Diameter Distribution
CoMoCAT Vs. HiPCO
Photo-luminescence
SEMICONDUCTING
TYBES ONLY

Courtesy –Prof. D. Resasco
COMoCAt: $(n,m)$ map, effect of gas feed at 800 °C on the produced SWNT.

$(n,m)$ map, effect of temperature and support morphology on the produced SWNT.

Alcohol CCVD on Catalysts Supported with Zeolite

Alcohol
- Ethanol
- Methanol

Electric Furnace

Simple, High-Purity Low-Temperature (550-900°C)

2.5/2.5 : Fe/Co (wt%) on USY Zeolite 30mg

Shinohara & Nagy 7.4[Å]

Raman shift (cm⁻¹)

Intensity (arb. units)

(a) 600°C
(b) 700°C
(c) 800°C
(d) 900°C
(e) Laser–oven

**ACCVD Chirality - Semiconducting**

Carbon source: Ethanol, CVD time: 10min

S. Maruyama et al.

Resasco's CoMoCAT

650°C

750°C

850°C
Comparison of DIPS and CoMoCat

Semiconducting

DIPS – Fe catalyst

Courtesy Prof. S. Iijima
Floating Catalyst – Fe/Co Chirality

HUT as measured with TEM/ED
BOTH Metallic and Semiconducting

HiPCO semiconducting from fluorescence
(n,m) Determination with Nanoprobre Electron Diffraction - Tilt Angle needs to be considered

Simulation of (23,10) at $\tau = 10^\circ$

courtesy Dr. Hua Jiang

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ (pixels)</th>
<th>$2d_3$ (pixels)</th>
<th>$2\xi_3$</th>
<th>$\tau(3)$</th>
<th>$2d_5$ (pixels)</th>
<th>$2\xi_5$</th>
<th>$\tau(5)$</th>
<th>$n^t$</th>
<th>$n$</th>
<th>$\varepsilon(n)$</th>
<th>$m^t$</th>
<th>$m$</th>
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<tbody>
<tr>
<td>Experimental</td>
<td>4.67</td>
<td>97.58</td>
<td>20.895</td>
<td>9.92</td>
<td>172.8</td>
<td>37.002</td>
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<td>23</td>
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<td>10.27</td>
<td>10</td>
<td>0.27</td>
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<tr>
<td>Simulation</td>
<td>10.44</td>
<td>218</td>
<td>20.881</td>
<td>9.70</td>
<td>366</td>
<td>36.973</td>
<td>10.21</td>
<td>23.28</td>
<td>23</td>
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<td>10.25</td>
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<td>163</td>
<td>16.092</td>
<td>10.84</td>
<td>23.28</td>
<td>23</td>
<td>0.28</td>
<td>10.25</td>
<td>10</td>
<td>0.25</td>
</tr>
</tbody>
</table>
Individual SWCNT*s onto substrates at $T_{ambient}$

Carbon arc-discharge
Laser ablation
HiPCO process

Substrate Chemical Vapour Deposition

Surfactants, Polymers, etc Functionalization

Bundles of CNTs (HiPco)

High growth temperature (500 °C)
Difficult integration in devices
Temperature sensitive substrates can not be used
SWCNT’s in Future NanoElectronics Applications

World wide economic activity associated with electronics:
(Phaedon Avouris, IBM, 3/2006)
- Semiconductors 215 B$
- Electronics 1 T$
- IT enabled services 5 T$

ISSUES TO BE SOLVED:

individual SWCNT with given (n,m) at ambient T to exact location at substrate
i.e.
how to integrate SWCNT’s into electronics integrated manufacturing processes

CNT transistor
- Advantage-
  - High speed operation is expected.
    \[ g_m \sim 10000 \mu S/\mu m^1 \text{ (p-Si x \sim 20)} \]
  - Excellent durability to large current density.
    \[ 10^9 \sim 10 A/cm^2 \text{ (Si x \sim 100)} \]
  - Compatible with high-\( \kappa \) gate oxides.
    HfO_2^1), SrTiO_3^2)
  - Low cost substrate can be used.
    Polymer^3)

Nihey et al, JJAP 2004

From Ishida et al., NEC, NT05
Schematic presentation of mechanism of CNT formation – control of bundling and charging?

Experimental set up

Reminder: DMA can classify only charged aerosol particles

Filter out electrical charged aerosol particles

Decomposition and charactristics of organoclay:
10-10000 V

Experimental set up

Filter out electrical charged aerosol particles

Decomposition and charactristics of organoclay:
10-10000 V
Carbon nanotubes are naturally charged (equally positively and negatively)
Bundled carbon nanotubes can host up to 8 elementary charges.
Bundled nanotubes are electrically charged regardless reactor temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>N(^{+/–}) (%)</th>
<th>N(^+) (%)</th>
<th>N(^–) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>99</td>
<td>47</td>
<td>53</td>
</tr>
<tr>
<td>800</td>
<td>99</td>
<td>48</td>
<td>52</td>
</tr>
<tr>
<td>900</td>
<td>97</td>
<td>41</td>
<td>59</td>
</tr>
</tbody>
</table>

Charged fraction (N\(^{+/–}\)) of CNTs at different reactor temperatures. (N\(^+\)) and (N\(^–\)) indicate the polarity distribution of charged CNTs.
Possible charging mechanisms

Surface reactions?

Energy dissipation?

Excitation of lattice vibration (phonons)

Electronic excitations (electrons, photons, ions)

Bundling process

Energy
1 eV/nm

Ion-emission via dissipation of the van der Waals energy released during nanotube bundling?

(10,10) Armchair nanotubes

D. J. Auerbach, Science, 21, 294, 2001
Higher CO – more clusters – higher NT concentration

Higher charged fraction

Higher heating power - more clusters – higher NT concentration

Higher charged fraction
Collection of electrically neutral CNTs (i.e. ESF on)

Minimum heating power (16 W)

53 % CO concentration  $\rightarrow$ Charged fraction $N^{+/\pm}=0$

Individual single-walled carbon nanotubes
• HWG method for the synthesis of single-walled CNTs

• Spontaneous electrical charging of bundled CNTs

• Individual CNTs remain electrically neutral

Applicability

Deposition of individual CNTs at ambient temperature on any solid substrate
Selective deposition of individual CNTs at ambient temperature on substrates by electrophoresis/thermophoresis

Epoxy-based substrate (MT=300 °C)
Temperature sensitive substrate

SiO$_2$(260 nm)/Si
Collaboration

Dr. Albert G. Nasibulin (aerosol synthesis of CNTs)
Dr. Hua Jiang (HR-TEM, ED/TEM)
Dr. David P. Brown (combined aerosol-CFD modelling)
Dr. David Gonzalez (charging of CNT’s)
Dr. Paula Queipo (cluster-catalyzed surface CVD synthesis of CNTs)
Prof. Sergei D. Shandakov (Marie Curie Fellow 2006-07, high yield synthesis)
Andrei Ollikainen, Anton Anissimov (growth and applications in electronics)

Prof. Daniel E. Resasco, Oklahoma U., USA (CVD growth & chirality)
Prof. David Tomanek, Michigan State U., USA (atomic modelling)
Dr. Peter V. Pikhitsa, Odessa Nat. Univ., Ukraine (SWCNT Nucleation)
Prof. Risto Nieminen, Dr. Arkady Kraseninnikov, COMP/HUT Finland (atomic modelling)
Dr. Bernd Freitag, FEI, Netherlands (C_s-TEM imaging)

Funding
* Academy of Finland via TULE program/ELENA Consortium
* EU FP5 RTN NanoCluster
* EU FP6 Marie Curie Fellow
* TEKES FinNano & MASI Programs

Tutorial Material
Dr. A. Loiseau, Prof. S. Maruyama, Prof. M. Endo, Prof. S. Iijima, Prof. K. Bolton, Prof. S. Farhat, Dr. C.D. Scott, Dr. Chris Kingston
Schematic presentation of mechanism of CNT formation

Simultaneous Synthesis of Fullerenes?

YES — submitted & to be presented later