Experimental and Molecular Dynamics Studies Related with Carbon Nanotubes

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What is Carbon Nanotube?

Chirality and Radius of SWNT

STM Image of Individual Atoms

TEM Pictures of SWNT Ropes
**Discovery of Carbon Nanotubes**

Discovery of MWNT: Iijima (1991)
Discovery of SWNT (Co-Fe): Iijima (1993)
MWNT by CVD
Macroscopic Prod. SWNTs (Ni-Co): Smalley (1996)
Arc Production (Ni-Y): Journet et al. (1997)
SWNT by CVD catalytic growth from metal particle
Field Emission, AFM Tip, Hydrogen Adsorption

**Applications of Nanotubes**

- Nanowires
- FET
- Biosensor
- Tips of AFM
- Fuel Cell Electrode
- H₂ Storage
- Mechanical

**Field Emission**

**Generation of SWNTs**

**Laser-Oven SWNT Generator**

**Laser-Oven Nanotube Generator**

Temperature

- 532 nm 53 %
- 532 nm 26 %
- 532 nm 1 %

TEM from Smalley et al. at Rice University
He gas
Power(+)
Power(-)
Graphite Electrodes
Stepping motor
Vacuum pump
Arc-Discharge Generator

SEM Image of Purification
Amorphous Carbon
Bundle of Tubes
Original
Purified

Catalytic CVD Generation of SWNTs

CCVD (Catalytic Chemical Vapor Deposition)

The HiPco Process
Single walled carbon nanotubes (swnt) from Hi pressure CO (Pco)

TEM
Raman
MgO supported Metal
1000 °C, methane

Self-Oriented Arrays of MWCNTs by CCVD (H. Dai’s Group at Stanford)

J.-F. Colomer, C. Stephan, S. Lefrant, G. V. Tendeloo, I. Willems, Z. Konya, A. Fonseca, Ch. Laurent, J. B. Nagy
CPL (2000)

Single walled carbon nanotubes (swnt) from Hi pressure CO (Pco)

R. E. Smalley
CNL
$500/gram
Rice University
New Catalytic CVD Generation of SWNTs

Experimental Technique

**Catalysts**

(CH$_3$CO$_2$)$_2$Fe
(CH$_3$CO$_2$)$_2$Co-4H$_2$O

**Supports**

Zeolite USY
HSZ-390HUA

C source
vacuum

Electric Furnace

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

C source vacuum

SEM Image

TEM Image

TEM Image

Raman Spectra (488nm)

Raman Spectra (488nm)

$D$ (nm) = $\frac{248}{\omega (\text{cm}^{-1})}$

Laser vaporization condition

Rod Ni/Co 0.6 at.%
Ar gas 50sccm
Temperature 1130℃

$\omega = \frac{\pi}{
\sqrt{\frac{2}{3}} \left( \frac{d}{a} \right)}$
Temperature Dependence

![Temperature Dependence Graph]

Generation mechanism of SWNTs

![Generation mechanism of SWNTs Diagram]

Model by Yudasaka et al., JPC B (1999)

Model by Kataura et al., Carbon (2000)

Total Energy $E_T$

$$E_T = \sum_{i,j} V_{ij}(r_{ij})$$

where $V_{ij}(r_{ij})$ is the interatomic potential function between atoms $i$ and $j$. The potential function is given by:

$$V_{ij}(r_{ij}) = \begin{cases} 
  -\frac{1}{2} \alpha \left( \frac{r_{ij}}{\delta} \right)^{12} & \text{for } \delta < r_{ij} < \delta + \frac{\delta}{2} \\
  -\frac{1}{2} \alpha \left( \frac{\delta}{2} \right)^{12} & \text{for } r_{ij} < \delta \\
  0 & \text{otherwise} 
\end{cases}$$

Potential parameters:

- $D_s = 6.325 \text{ eV}$
- $S = 2.72$
- $\delta = 0.80469$
- $\beta = 0.011304$
- $\gamma = 1.5 A^{-1}$
- $\delta' = 2.5 A$


C-C Potential Function

$E_B \equiv V_g + V_r + V_C$

where $V_r$ is the repulsive term, $V_g$ is the attractive term, and $V_C$ is the Coulomb term.

Model by Kataura et al., Carbon (2000)

Potential parameters:

- $D_s = 6.325 \text{ eV}$
- $S = 1.29$
- $\beta = 1.5 A^{-1}$
- $R_s = 1.315 A$
- $R_L = 2.0 A$


M-C and M-M Potential Function Expression

$E_B = E_g + E_r + E_C$

where $E_g$ is the repulsive term, $E_r$ is the attractive term, and $E_C$ is the Coulomb term.

Snapshots of Clustering Process at 6000 ps
2500 carbon atoms & 25 Ni atoms
Control temperature $T_c = 3000$ K, 585 Å Cubic Box

Snapshots of Annealing Process for NiC$_{60}$

Cluster Source Nozzle for FT-ICR

FT-ICR (Fourier Transform Ion Cyclotron Resonance) Mass Spectrometer

Negative Clusters

Isotope Distribution

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$</td>
<td>100%</td>
</tr>
<tr>
<td>C$_{60}$H</td>
<td>50%</td>
</tr>
<tr>
<td>C$_{55}$Co</td>
<td>40%</td>
</tr>
<tr>
<td>C$_{55}$Ni</td>
<td>40%</td>
</tr>
<tr>
<td>C$_{50}$NiCo</td>
<td>35%</td>
</tr>
</tbody>
</table>
The Way to Nanotube?

Collisions 2000K, Slower Rate of Shrinking

2000K

3000K

Enlarged View

Generation Model of SWNTs

Electric Furnace

Ar Flow 0.8 cm/s, 500 Torr

Evaporation ~ 1.7 µg/pluse

Ni/Co Loaded Graphite

200~500 µs

2cm

3ms~1s

Molecular Dynamics Simulations Related to SWNTs

FUEL CELLS (PEFC)

Distributed power supply

Supply of hydrogen

Automobiles

Mobile machines

Storage problems for small light-weighted fuel cells

Methanol

Liquid hydrogen

High pressure gas

Metal hydride

Carbon materials

Fuel Cell and Hydrogen Storage

FUEL CELLS

Distributed power supply

Automobiles

Mobile machines

Energy Density of Hydrogen

Initial Configuration for (10,10) SWNTs

3504 Hydrogen Molecules

9504 Hydrogen Molecules

3080 C atoms

7 SWNTs Bundle (440 C atoms each)

Snapshots of Absorption for (10,10) SWNTs

Phase Transformation

(a) 12 MPa
(b) Transformed
(c) 6 MPa
(d) Transformed

Snapshots for Various SWNTs

(10,10) (16,16)
Close Packed
6.1 wt %
7.2 wt %
Interstially Filled
7.5 wt %
8.6 wt %

Measurement of an Isolated MWNT

Heat Conduction

Simulation Technique

Without the Periodic Boundary Condition!!

\[ m \dot{\mathbf{x}} = f_{\text{int}} + f_{\text{phantom}}(\sigma) + \alpha \dot{\mathbf{x}} \]
\[ \sigma = \sqrt{2akT_c / N} \]
\[ \alpha = \frac{m \pi}{6} \omega \nu, \quad \omega \nu = k_B T / h \]
\[ \theta_s = 2230K \ (	ext{Diamond}) \]
Temperature Distribution along a Nanotube

![Temperature Distribution](image)

Thermal Conductivity Better than Diamond?

Effect of nanotube length

![Effect of nanotube length](image)

Phonon Dispersion Relations (5,5)-101nm

![Phonon Dispersion Relations](image)

Peapod (Fullerene@Nanotube)

![Peapod](image)
Snapshots of Peapod to Double-walled Carbon Nanotube at 3000K.