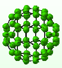
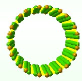
Colloquium Micro/Nano Thermal Engineering @ Seoul, 2002/2/18

Experimental and Molecular Dynamics Studies Related with Carbon Nanotubes





Shigeo Maruyama

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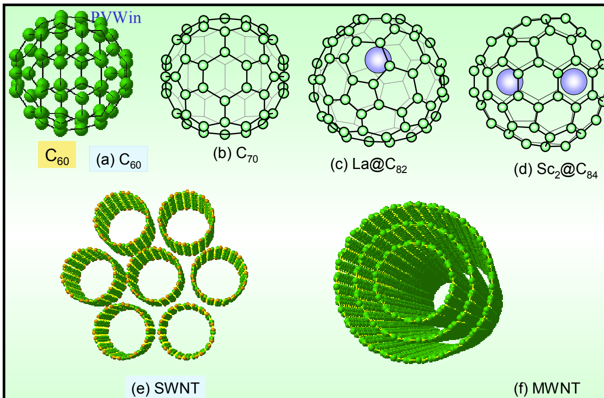
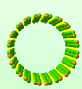
http://www.photon.t.u-tokyo.ac.jp/~maruyama/
E-mail: maruyama@photon.t.u-tokyo.ac.jp

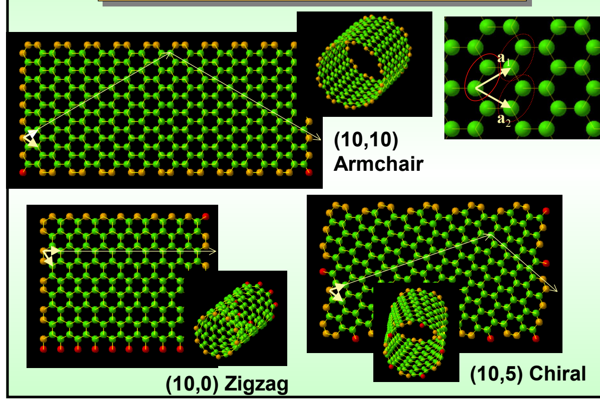


Typical Structures of Fullerene & Nanotubes

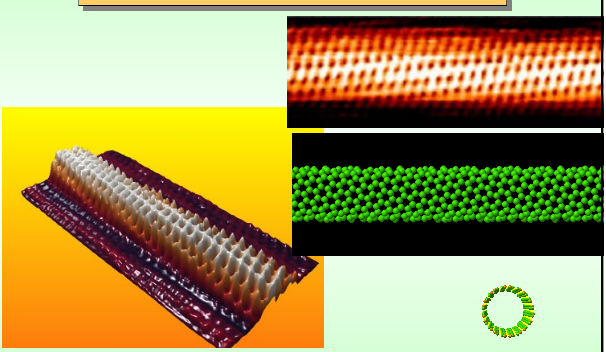
What is Carbon Nanotube?



Chirality and Radius of SWNT

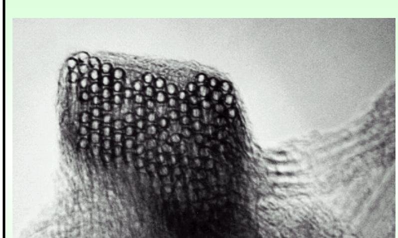


STM Image of Individual Atoms

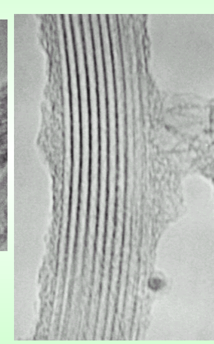


http://vortex.tn.tudelft.nl/~dekker/nanotubes.html

TEM Pictures of SWNT Ropes



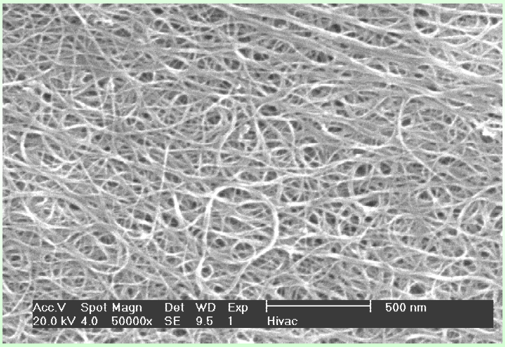
About 100 SWNTs



Individual tube diameter: 1.3 nm
Spacing: 0.34 nm
Misalignments and Terminations

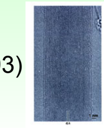
TEM from Smalley et al. at Rice University

Bucky Paper (A Tangle of Ropes)



R. E. Smalley at Rice University

Discovery of Carbon Nanotubes



Discovery of MWNT: Iijima (1991)

Discovery of SWNT (Co-Fe): Iijima(1993)

MWNT by CVD

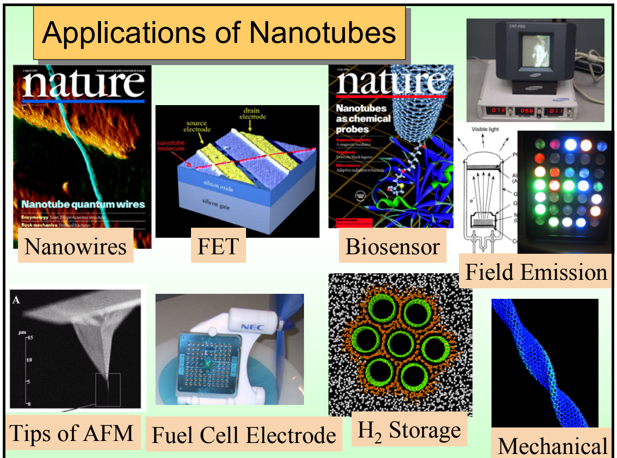
Macroscopic Prod. SWNTs (Ni-Co): Smalley (1996)

Arc Production (Ni-Y): Journet et al. (1997)

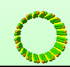
SWNT by CVD catalytic growth from metal particle

Field Emission, AFM Tip, Hydrogen Adsorption

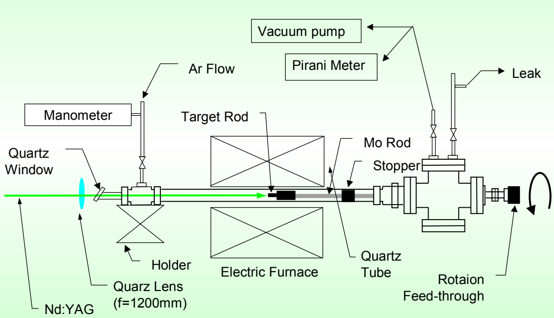
Applications of Nanotubes



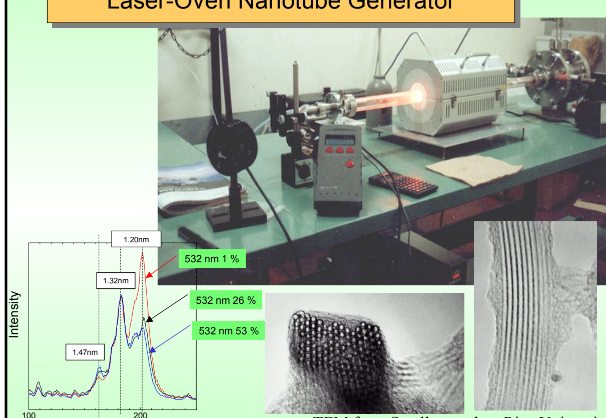
Generation of SWNTs



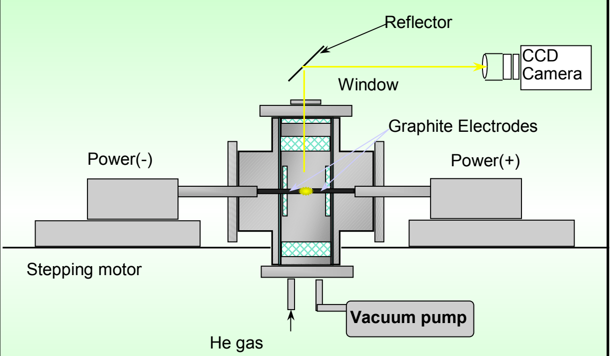
Laser-Oven SWNT Generator



Laser-Oven Nanotube Generator

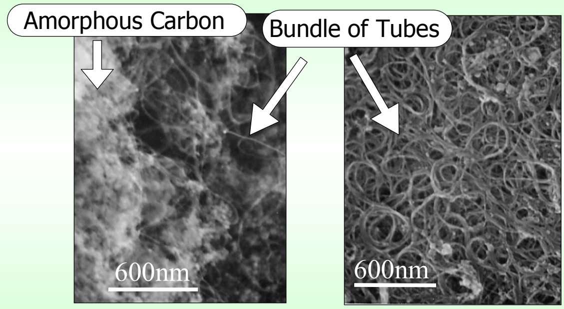


TEM from Smalley et al. at Rice University



Arc-Discharge Generator

SEM Image of Purification



Original ➡ Purified

Catalytic CVD Generation of SWNTs

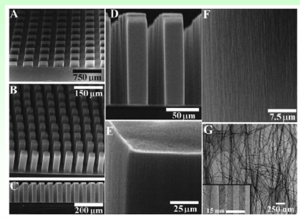


Fig. 2. Electron micrographs of self-oriented nanotubes synthesized on n^+-type porous silicon substrates. (**A**) SEM image of nanotube blocks synthesized on 250 µm by 250 µm catalyst patterns. The nanotubes are 80 µm long and oriented perpendicular to the substrate [see (F)]. (**B**) SEM image of nanotube towers synthesized on 38 µm by 38 µm catalyst patterns. The nanotubes are 130 µm long. (**C**) Side view of the nanotube towers in (B). The nanotubes self-assemble such that the edges of the towers are perfectly perpendicular to the substrate. (**D**) Nanotube "twin towers," a zoom-in view of Fig. 2C. (**E**) SEM image showing sharp edges and corners at the top of a nanotube tower. (**F**) SEM image showing that nanotubes in a block are well aligned to the direction perpendicular to the substrate surface. (**G**) TEM image of pure multiwalled nanotubes in several nanotube blocks grown on a n^+-type porous silicon substrate. Even after ultrasonication for 15 min in 1,2-dichloroethane, the aligned and bundled configuration of the nanotubes is still evident. The inset is a high-resolution TEM image that shows two nanotubes bundling together. The well-ordered graphitic lattice fringes of both nanotubes are resolved.

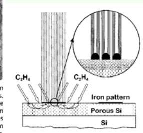
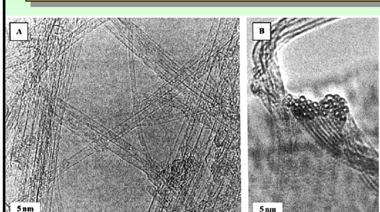
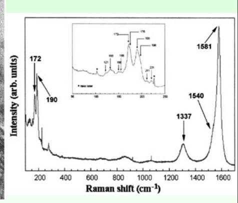


Fig. 3. Nanotube growth and self-orientation on porous silicon substrate. On the substrate, the iron oxide nanoparticles remain pinned down during CVD growth, and thus base growth operates. The ethylene gas molecules feed the growing nanotubes at the edge of the catalyst square by diffusing through the nanotubes and through the porous silicon layer. On a plain silicon substrate, the ethylene molecules can only feed the edge of the catalyst square and diffuse through the nanotubes, which results in a growth rate lower than would be observed on a porous silicon substrate (*28*). The nanotubes within each block interact via van der Waals forces, which provide the overall rigidity for oriented growth. Some openings exist between bundled nanotubes, allowing gas to diffuse.

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

CCVD (Catalytic Chemical Vapor Deposition)





TEM

Raman

MgO supported Metal

1000 °C, methane

Yields of SWNTs synthesis depending on the catalysts used

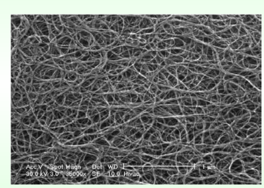
Metals used	Weight percent of metal	Yields for as prepared catalyst	Yields for hydrogenated catalyst
Co	2.5%	5.5%	5.7%
	5%	6.5%	4.7%
Fe	2.5%	6%	5.9%
	5%	5.8%	5%
Co–Fe	2.5–2.5%	7.6%	8.3%

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

The HiPco Process

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

1 step → Gas phase



$500/gram

R. E. Smalley
CNL
Rice University

New Catalytic CVD Generation of SWNTs

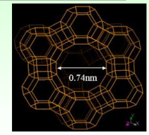
Experimental Technique

Catalysts

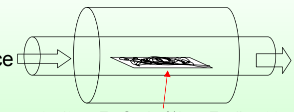
$(CH_3CO_2)_2Fe$
$(CH_3CO_2)_2Co\text{-}4H_2O$

Supports

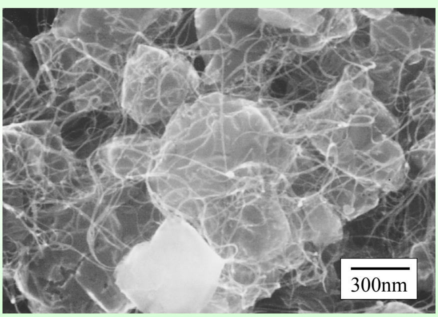
Zeolite USY
HSZ-390HUA



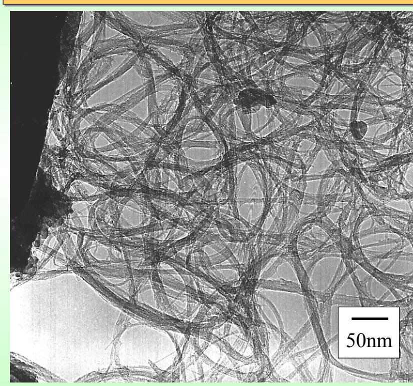
SiO_2 99.6 wt%
Al_2O_3 0.4wt%
SiO_2/Al_2O_3: 390.0



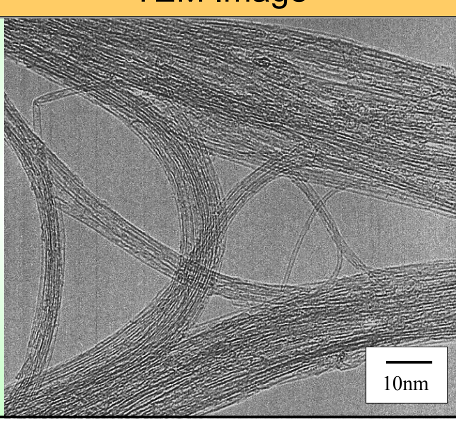
SEM Image



TEM Image



TEM Image

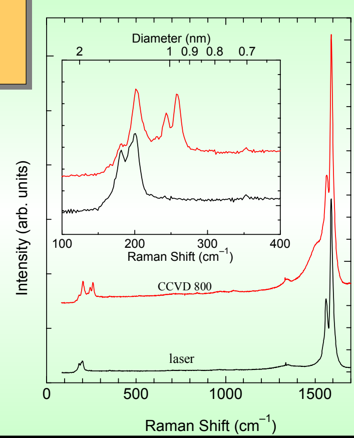


Raman Spectra (488nm)

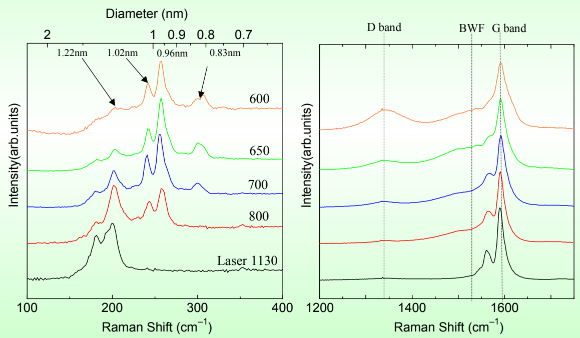
$$d\,(nm) = \frac{248}{\omega\,(cm^{-1})}$$

Laser vaporization condition

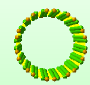
Rod	Ni/Co 0.6 at.%
Ar gas	50sccm
Temperature	1130℃



Temperature Dependence



Generation mechanism of SWNTs



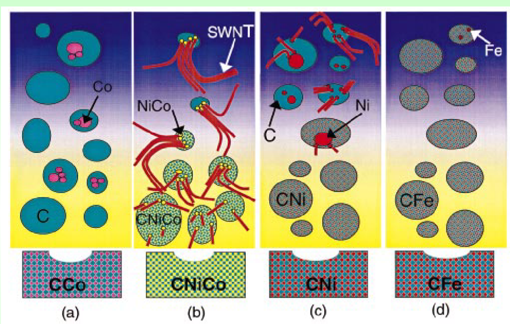


Figure 9. Drawings illustrating how the SWNT yield depends on metal species. The targets are (a) C_xCo_z, (b) $C_xNi_yCo_y$, (c) C_xNi_y, and (d) C_xFe_y.

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

Model by Kataura et al., Carbon (2000)

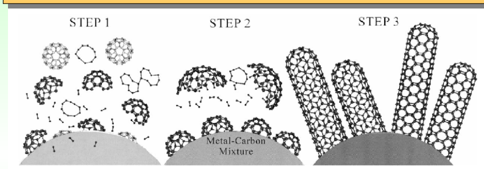
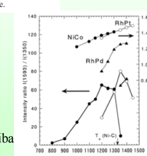


Fig. 5. A schematic picture of a growth model of SWNTs. Step 1: carbon clusters and fullerene caps are produced and eaten by metal particles. Step 2: metal particles stop to eat fullerenes and are covered with caps. Step 3: SWNTs grow using amorphous carbon. The temperature of the system decreases with increasing the 'step' number. In this model, the diameter distribution is determined by the diameter of caps at step 2 and then the SWNTs grow at step 3. The temperature of step 3 is very close to the furnace temperature.



H. Kataura , Y. Kumazawa , Y. Maniwa , Y. Ohtsuka , R. Sen , S. Suzuki ,Y. Achiba
Carbon 38 (2000) 1691-1697

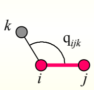
Total Energy E_b:

$$E_b = \sum_i \sum_{j(<i)} \left\{ V_R(r_{ij}) - B^*_{ij} V_A(r_{ij}) \right\}$$

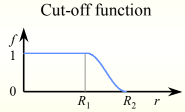
$$V_R(r) = f(r)\frac{D_e}{S-1}\exp\left\{-\beta\sqrt{2S}(r-R_e)\right\} \qquad V_A(r) = f(r)\frac{D_e S}{S-1}\exp\left\{-\beta\sqrt{\frac{2}{S}}(r-R_e)\right\}$$

$$B^*_{ij} = \frac{B_{ij}+B_{ji}}{2}, \quad B_{ij} = \left[1+\sum_{k(\neq i,j)}\left\{G_c(\theta_{ijk})f(r_{ik})\right\}\right]^{-\delta}$$

$$G_c(\theta) = a_0\left(1+\frac{{c_0}^2}{{d_0}^2}-\frac{{c_0}^2}{{d_0}^2+(1+\cos\theta)^2}\right)$$



Cut-off function



Potential parameters

$D_e =$	6.325eV	$S =$	1.29	$\beta =$	1.5Å^{-1}	$R_e =$	1.315Å
$\delta =$	0.80469	$a_0 =$	0.011304	$c_0 =$	19	$d_0 =$	2.5
$R_1 =$	1.7Å	$R_2 =$	2.0Å				

C-C Potential Function

From D. W. Brenner: *Phys. Rev. B*, **42**, 9458(1990)

$$E_{ij} = V_R + V_A + V_C$$

$f(r_{ij})$: cut-off function

V_R: Repulsive term

$$V_R = f(r_{ij})\frac{D_e}{S-1}\exp\left\{-\beta\sqrt{2S}(r_{ij}-R_e)\right\}$$

V_A: Attractive term

$$V_A = -f(r_{ij})\cdot B^*\frac{D_e S}{S-1}\exp\left\{-\beta\sqrt{2/S}(r_{ij}-R_e)\right\}$$

M-C

B^*: normalized bond order

$$B^* = \left\{1+b(N^{\mathrm{C}}-1)\right\}^{\delta}$$

N^{C}: carbon coordinate number

$$N^{\mathrm{C}} = 1+\sum_{\mathrm{carbon}\,k(\neq j)} f(r_{ik})$$

V_C: Coulomb term

$$V_C = -f(r_{ij})\frac{e^2}{4\pi\varepsilon_0}\frac{c_{\mathrm{C}}c_{\mathrm{M}}}{r_{ij}}$$

M-M

$$R_e(N_{ij}) = R_{e1} - R_{e2}\exp\left\{-C_R(N_{ij}-1)\right\}$$

$$D_e(N_{ij}) = D_{e1} + D_{e2}\exp\left\{-C_D(N_{ij}-1)\right\}$$

N^{M}_i: metal coordinate number

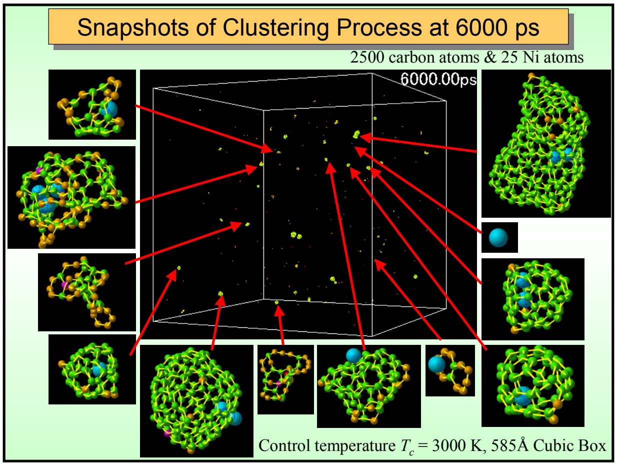
$$N^{\mathrm{M}}_i = 1+\sum_{\mathrm{metal}\,k(\neq j)} f(r_{ik}) \qquad N_{ij} = \frac{N^{\mathrm{M}}_i + N^{\mathrm{M}}_j}{2}$$

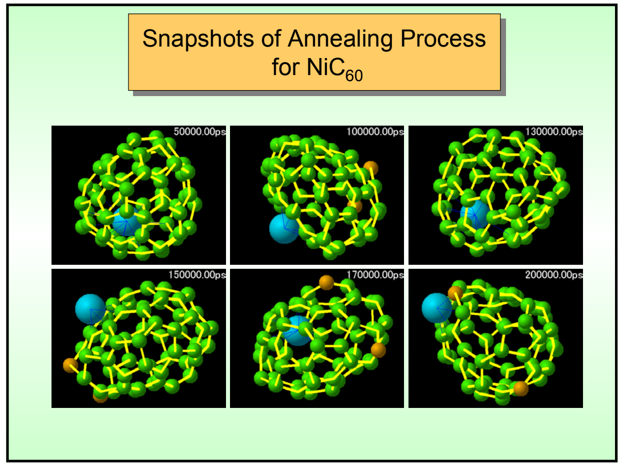
$$V_C = f(r_{ij})\frac{e^2}{4\pi\varepsilon_0}\frac{c_{\mathrm{M}i}c_{\mathrm{M}j}}{r_{ij}}$$

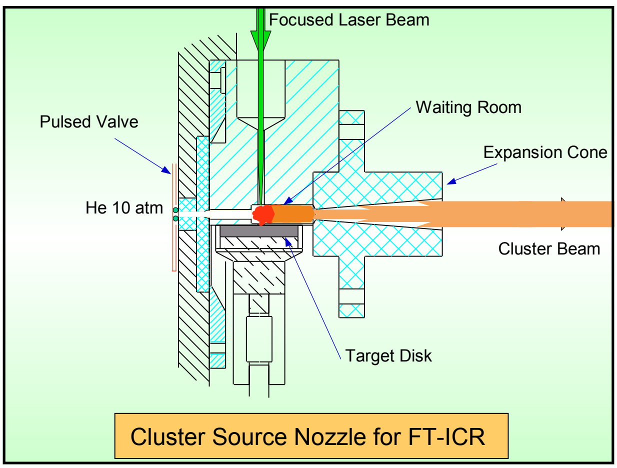
c_{M}, c_{C} : charge of M (+) and C(-)

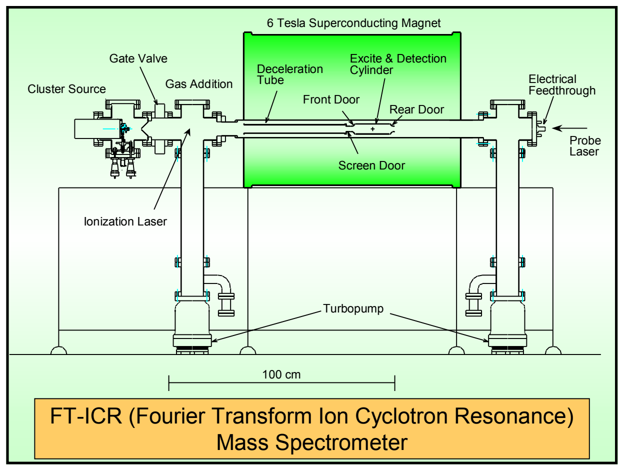
$$c_{\mathrm{M}} = 3-\exp(-k_1 N^{\mathrm{C}} + k_2) \qquad c_{\mathrm{C}} = c_{\mathrm{M}} / N^{\mathrm{C}}$$

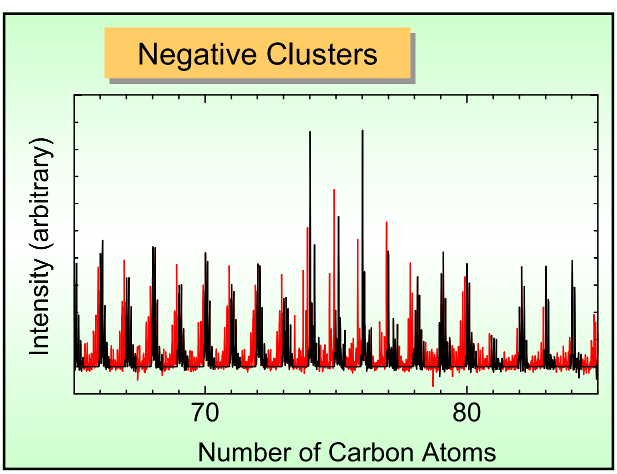
M-C and M-M Potential Function Expression

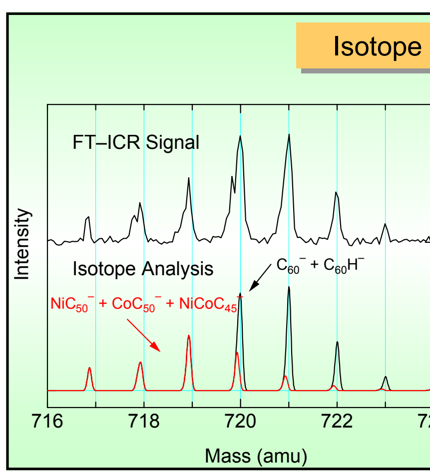




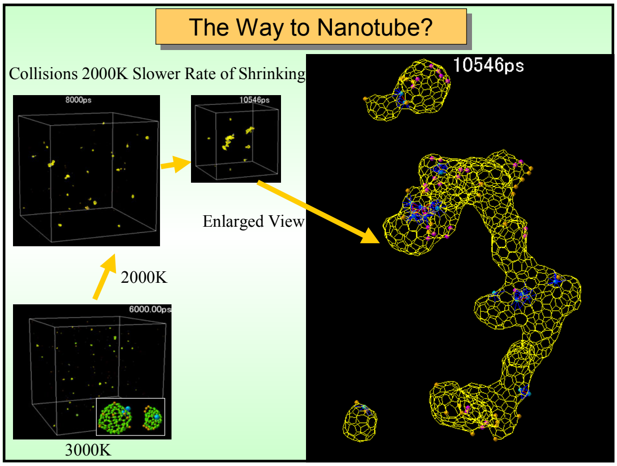


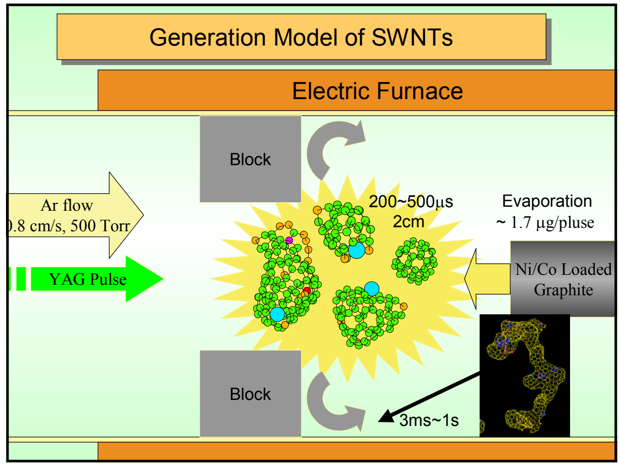


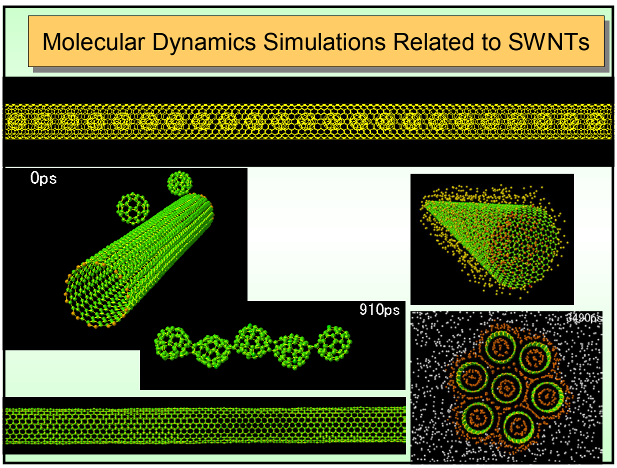




C60	100%
C60H	50%
C55Co	40%
C55Ni	40%
C50NiCo	35%







Fuel Cell and Hydrogen Storage

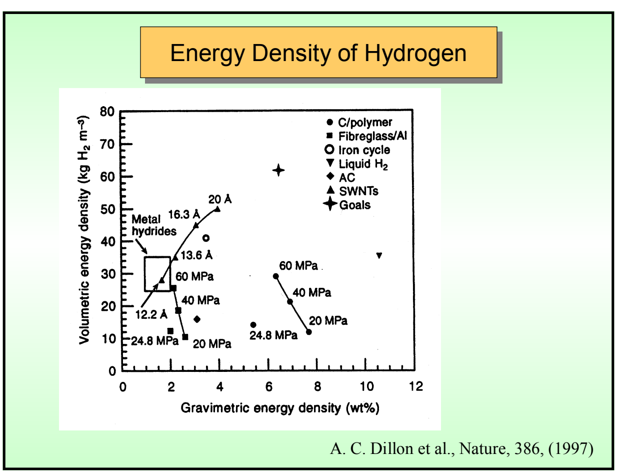
FUEL CELLS (PEFC)

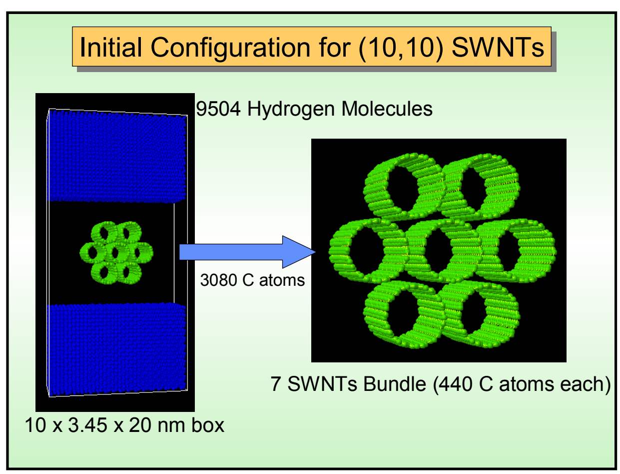
Distributed power supply
Automobiles
Mobile machines

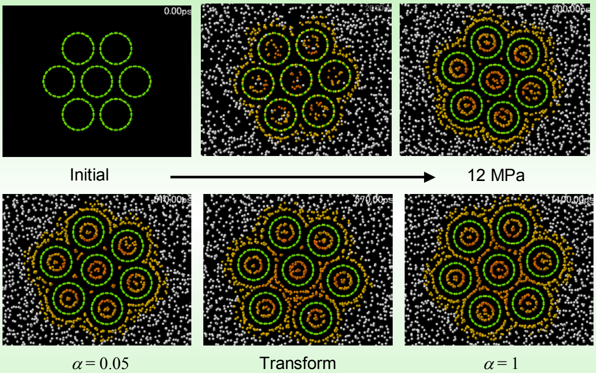
Supply of hydrogen

Storage problems for small light-weighted fuel cells

Methanol	Regenerator is heavy
Liquid hydrogen	Low temperature, Energy loss
High pressure gas	Weight of case
Metal hydride	Heavy
Carbon materials	

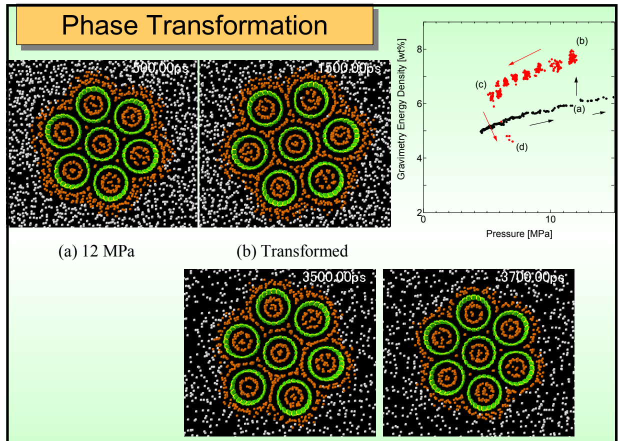






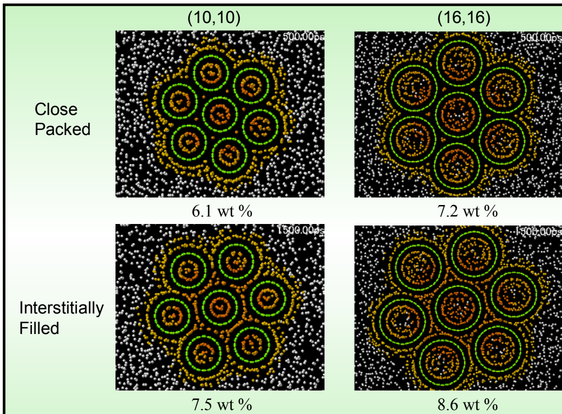
Snapshots of Absorption for (10,10) SWNTs

Phase Transformation



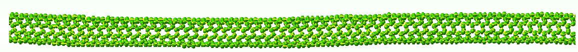
(a) 12 MPa (b) Transformed

(c) 6 MPa (d) Transformed

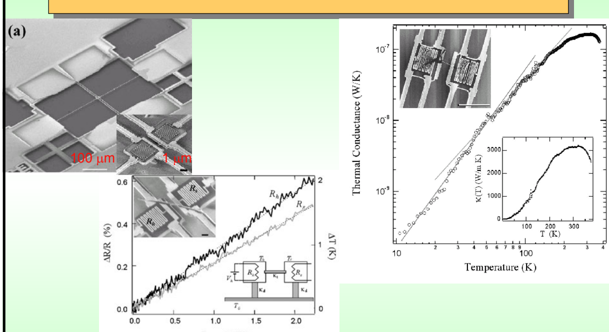


Snapshots for Various SWNTs

Heat Conduction



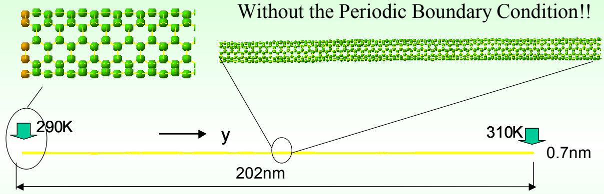
Measurement of an Isolated MWNT



P. Kim, L. Shi, A. Majumdar, P. L. McEuen, Thermal Transport Measurements of Individual Multiwalled Nanotubes, Los Alamos Natl. Lab., Prepr. Arch., Condens. Matter (2001), 1. → PRL 87, 215502-1 (2001)

Simulation Technique

Without the Periodic Boundary Condition!!

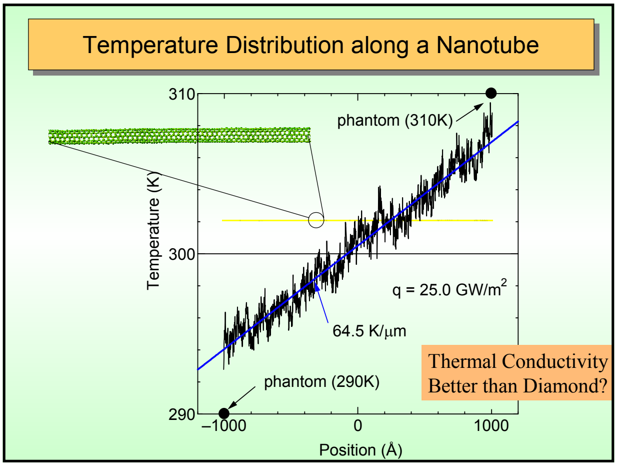


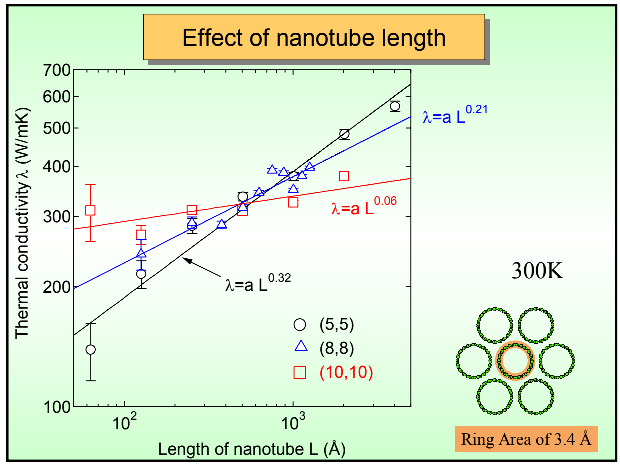
Temperature Control by Phantom Technique

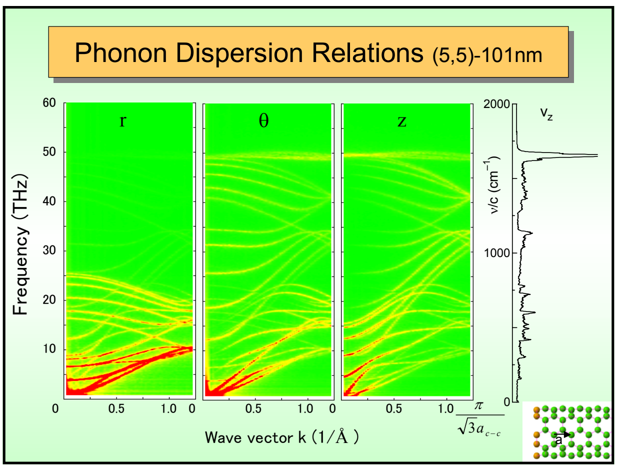
$$m\ddot{\mathbf{x}} = \mathbf{f}_{Pot} + \mathbf{f}_{Rand}(\sigma) - \alpha\dot{\mathbf{x}}$$

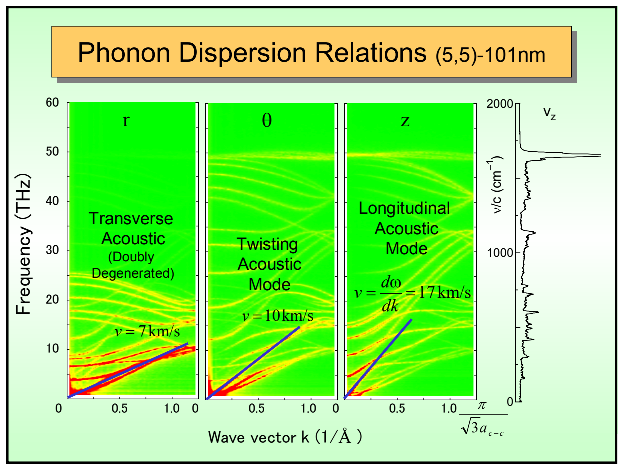
$$\sigma = \sqrt{2\alpha k_B T_C / \Delta t_S},\ \alpha = m\frac{\pi}{6}\omega_D,\ \omega_D = k_B\theta_D/\hbar$$

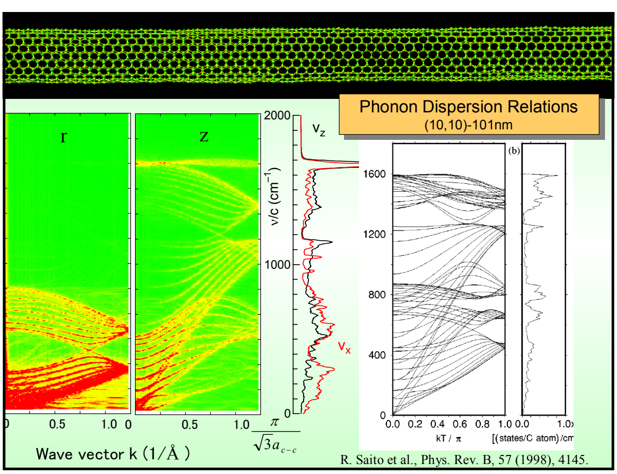
$$\theta_D = 2230\text{K (Diamond)}$$

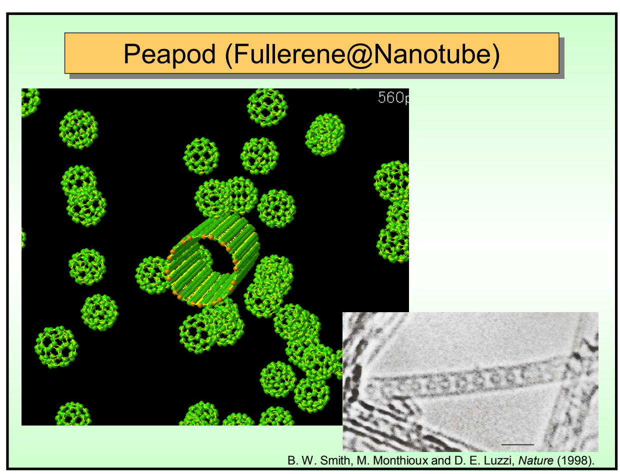

Temperature Distribution along a Nanotube
phantom (310K)
phantom (290K)
q = 25.0 GW/m2
64.5 K/μm
Thermal Conductivity
Better than Diamond?
Temperature (K)
310
300
290
–1000
0
1000
Position (Å)


Effect of nanotube length
Thermal conductivity λ (W/mK)
700
600
500
400
300
200
100
λ=a L0.21
λ=a L0.06
λ=a L0.32
(5,5)
(8,8)
(10,10)
300K
Length of nanotube L (Å)
Ring Area of 3.4 Å


Phonon Dispersion Relations (5,5)-101nm
Frequency (THz)
r
θ
z
vz
ν/c (cm−1)
2000
1000
Wave vector k (1/Å)


Phonon Dispersion Relations (5,5)-101nm
Frequency (THz)
r
θ
z
Transverse
Acoustic
(Doubly
Degenerated)
v = 7km/s
Twisting
Acoustic
Mode
v = 10km/s
Longitudinal
Acoustic
Mode
v = dω/dk = 17km/s
vz
ν/c (cm−1)
Wave vector k (1/Å)


Phonon Dispersion Relations
(10,10)-101nm
r
z
vz
vx
ν/c (cm−1)
Wave vector k (1/Å)
R. Saito et al., Phys. Rev. B, 57 (1998), 4145.


Peapod (Fullerene@Nanotube)
B. W. Smith, M. Monthioux and D. E. Luzzi, Nature (1998).

Snapshots of Peapod to Double-walled Carbon Nanotube

at 3000K