Carbon nanotube metrology for science and manufacturing

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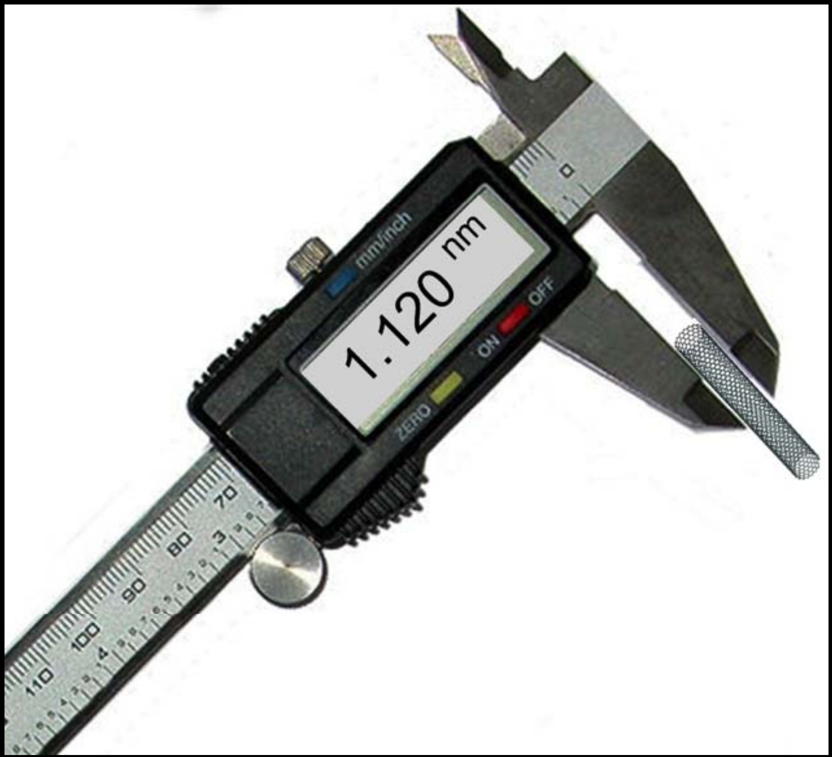
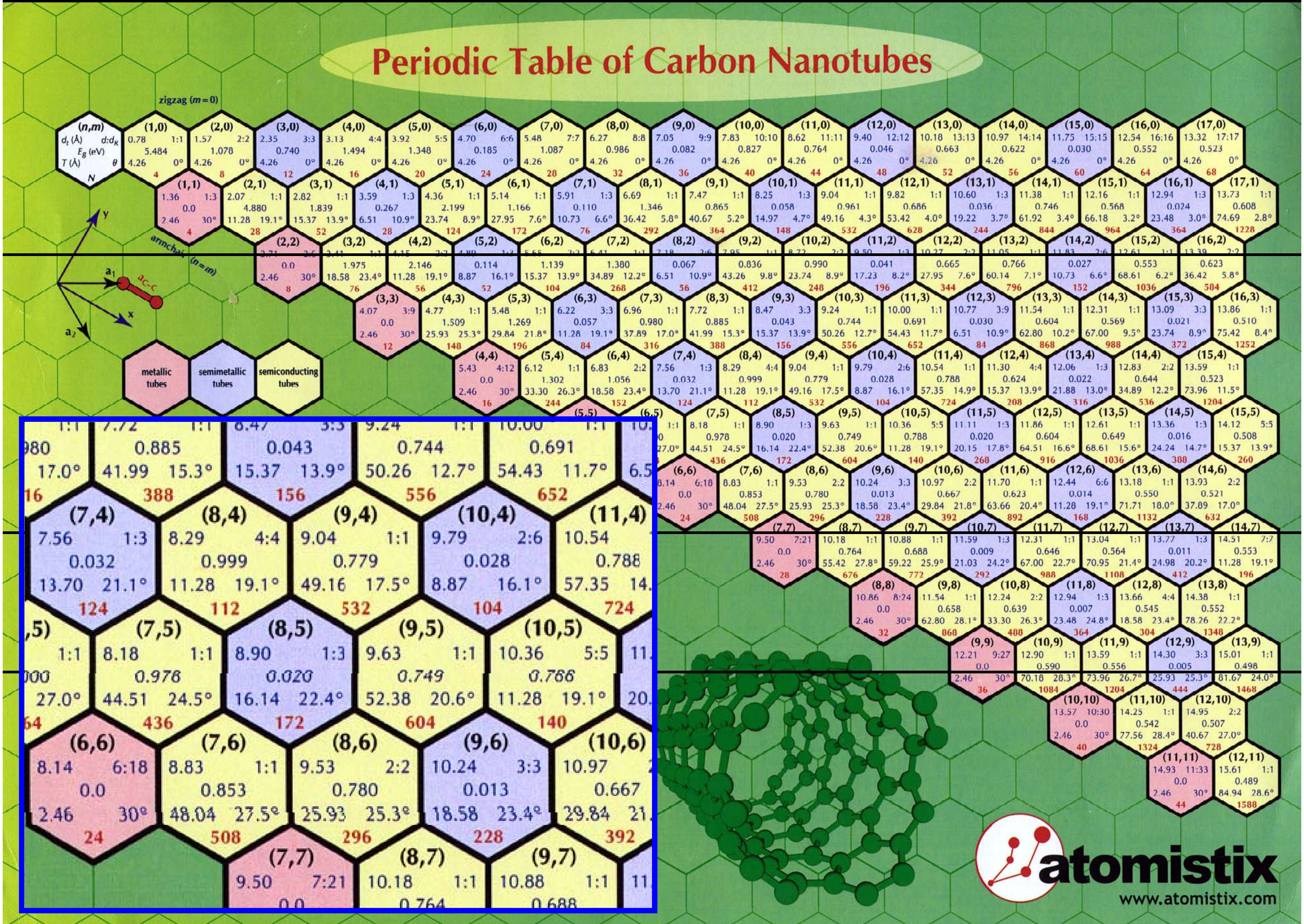
February 28, 2011

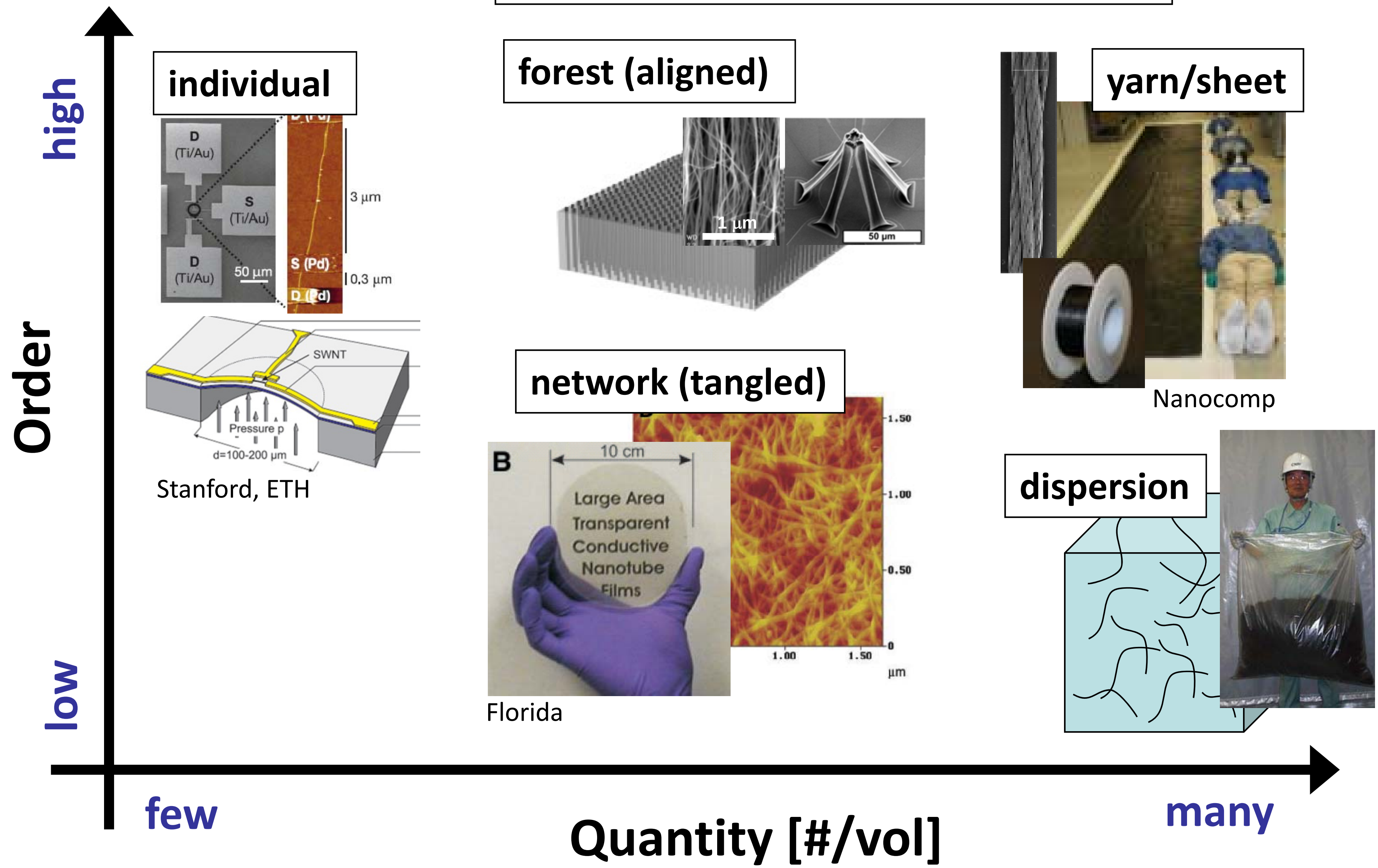




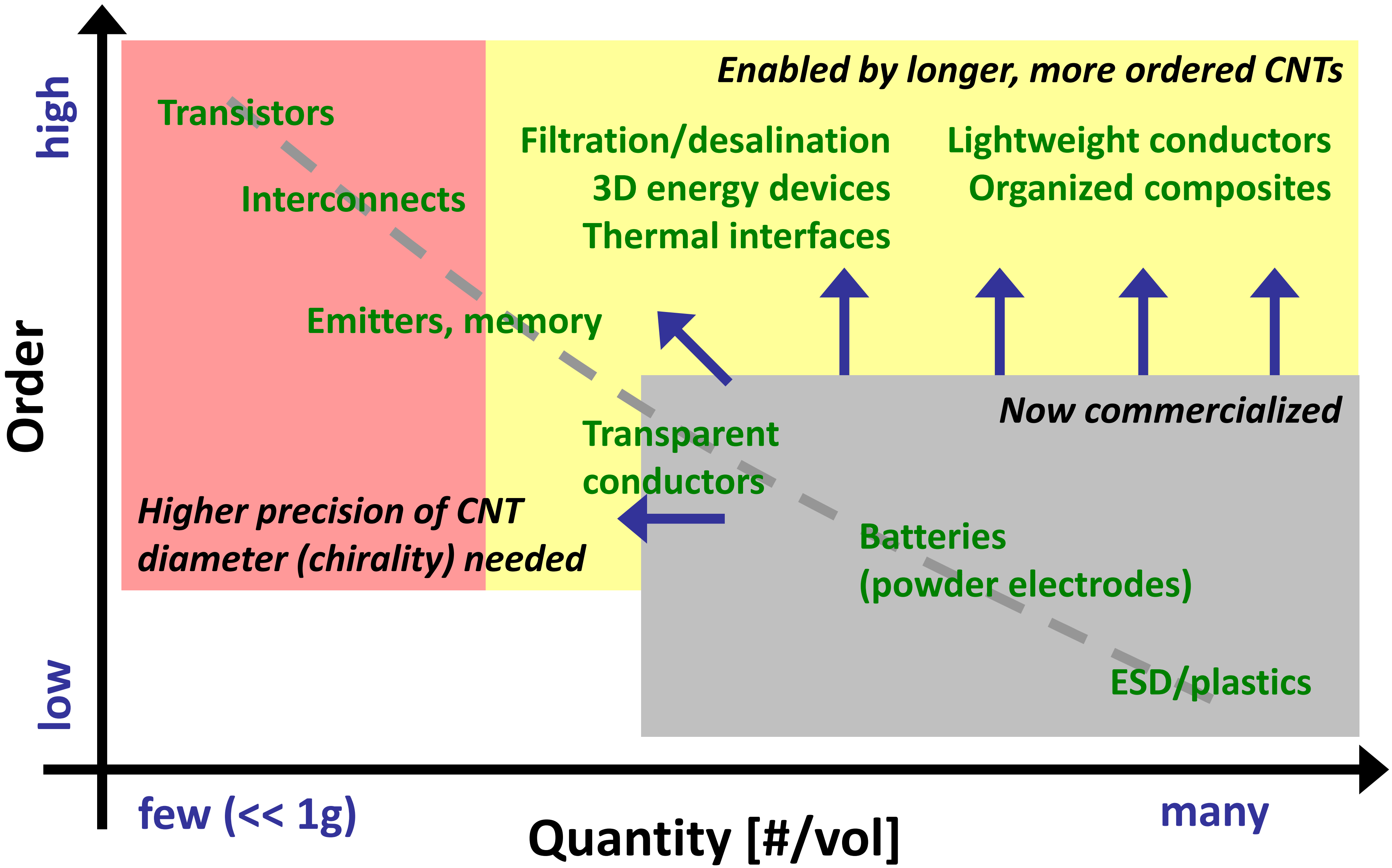
Periodic Table of Carbon Nanotubes
zigzag (m = 0)
armchair (n = m)
(n,m)
d_t (Å) d:d_R
E_g (eV)
T (Å) θ
N
metallic tubes
semimetallic tubes
semiconducting tubes
atomistix
www.atomistix.com

Configurations

Order = quality, purity, alignment
Quantity = #/volume



Applications



September 23rd and 24th 2010

Hosted by the National Institute of Standards and Technology

Gaithersburg, MD 20899

Organizing Committee

Stephen Freiman

Jeffrey A. Fagan

Stephanie Hooker

Kalman B. Migler

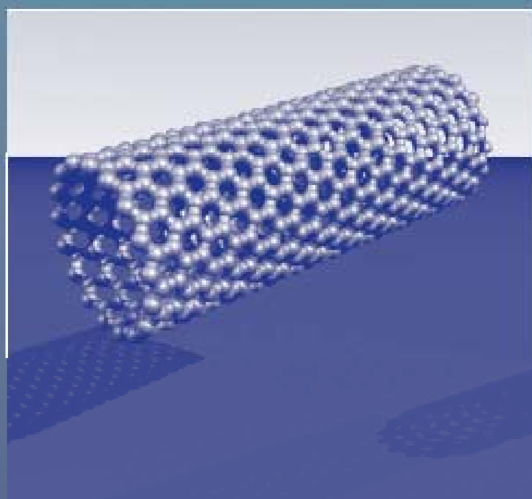
Angela R. Hight Walker

Ming Zheng

http://www.nist.gov/mml/polymers/complex_fluids/4th-carbon-nanotube-workshop.cfm practice guide

NIST recommended

Measurement Issues in Single Wall Carbon Nanotubes



Stephen Freiman
Stephanie Hooker
Kalman Migler
Sivaram Arepalli

NIST
National Institute of Standards and Technology
U.S. Department of Commerce

Special Publication 960-19

NIST Recommended Practice Guide

Special Publication 960-19

Measurement Issues in Single Wall Carbon Nanotubes

Edited by:
Stephen Freiman
Stephanie Hooker
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NIST Materials Science and Engineering Laboratory

and
Sivaram Arepalli
NASA-JSC

March 2008

U.S. Department of Commerce
Carlos M. Gutierrez, Secretary

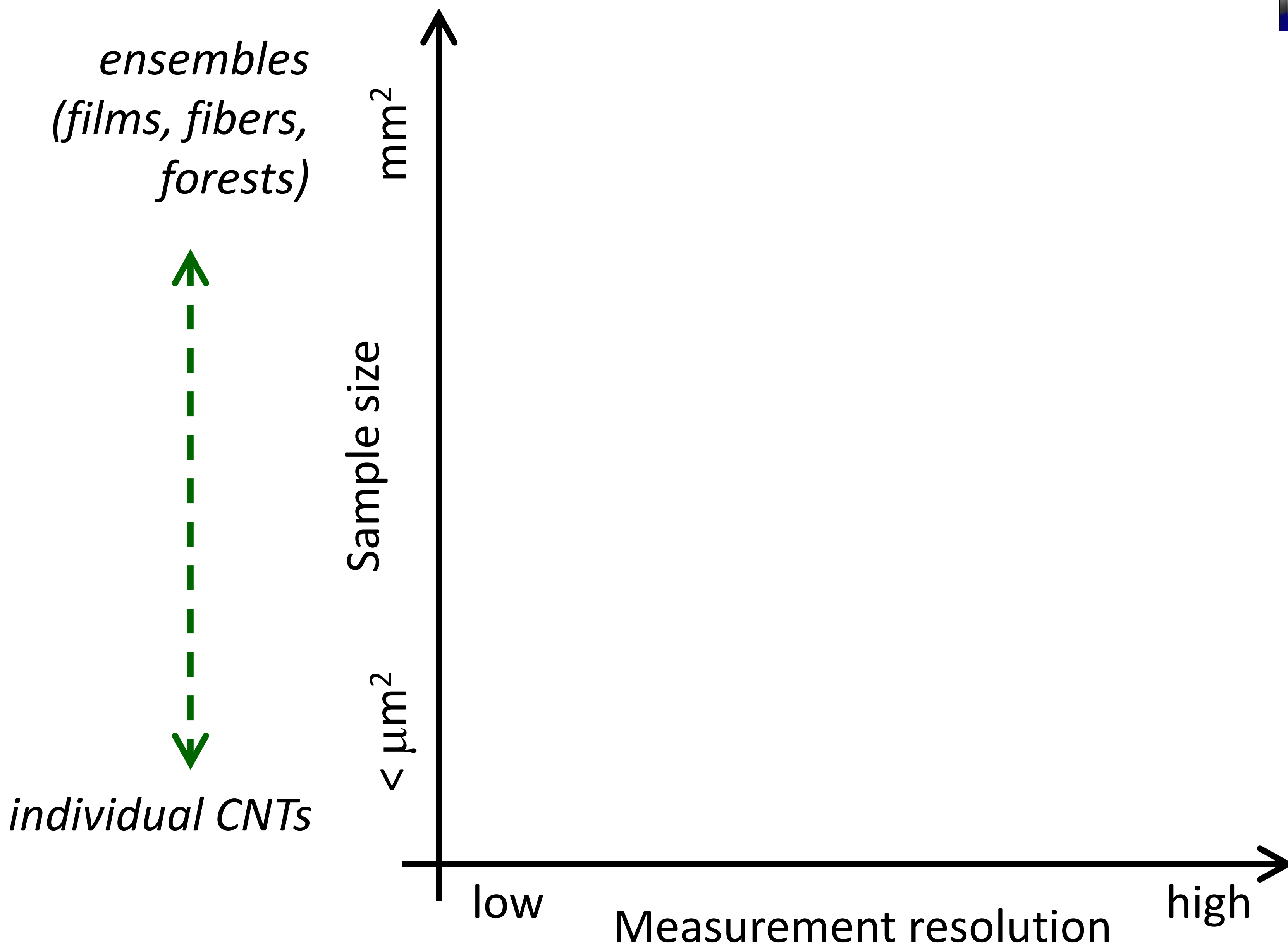
National Institute of Standards and Technology
Dr. James M. Turner, Acting Director and Deputy Director

RM 8281 is a set of dispersed nanotube populations with different average lengths; the set includes a long, medium and short fraction, as well as a 1 % (mass/volume) surfactant blank. A set contains a sealed, sterilized, ampule (~2.6 mL) of each component. These sets were produced using centrifugation based separation of a common parent dispersion produced from SRM 2483. Applications of these materials include fundamental research, instrument calibration, and EHS applications.

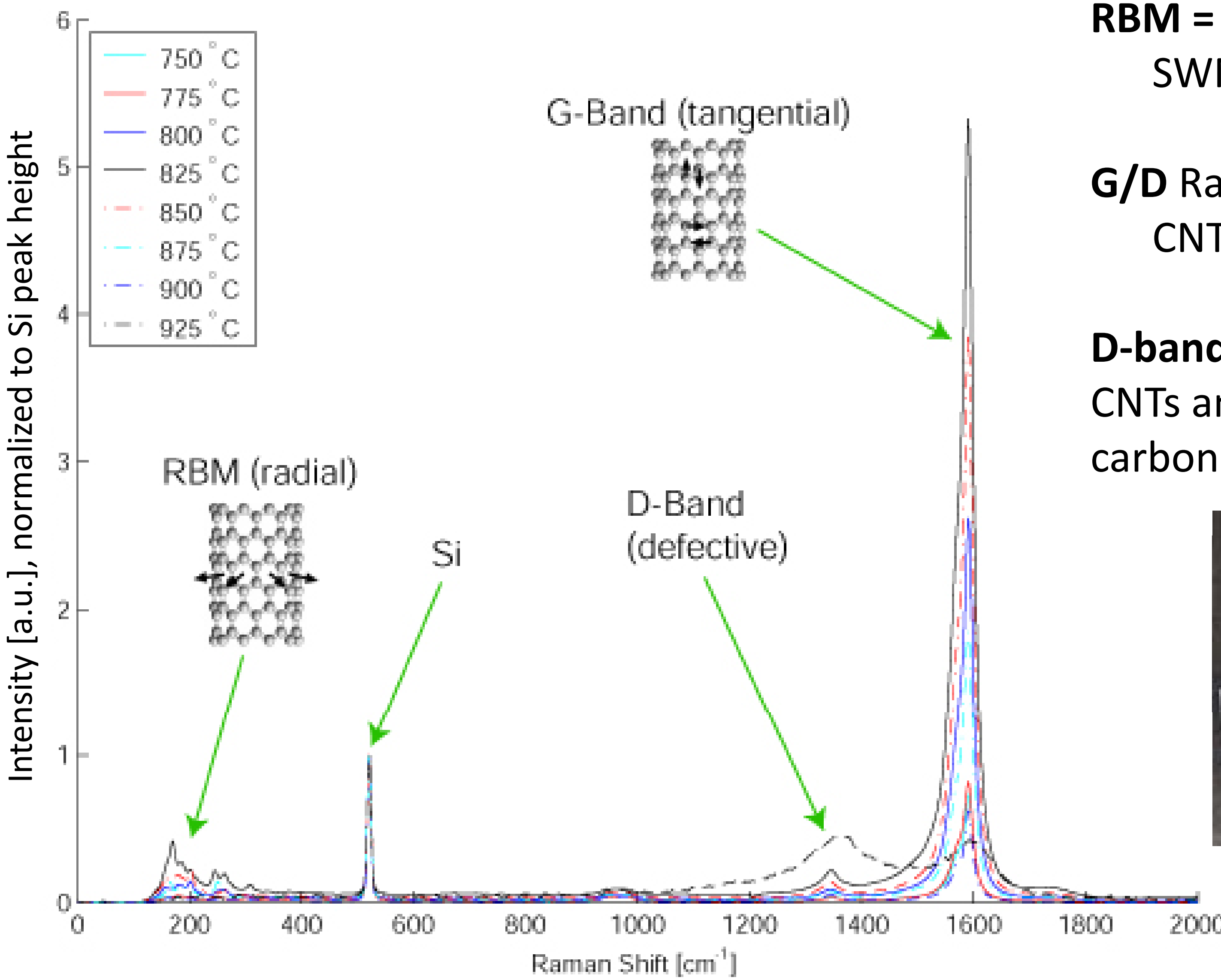
http://www.nist.gov/mml/polymers/complex_fluids/nanotube-reference-materials.cfm
http://www.nist.gov/mml/polymers/complex_fluids/4th-carbon-nanotube-workshop.cfm

CNT material measurements

- Structure
  - Diameter and chirality — TEM, AFM, Raman, Photoluminescence
  - Length — TEM, SEM
  - Quality (= defect density) — Raman, TEM, TGA
- Morphology
  - Bundling — SEM, TEM
  - Alignment — Optical polarization,
  - Connectivity/ends — X-ray scattering
- Chemistry
  - Purity; residual catalyst — TGA
  - Functionalization — IR spectroscopy
  - Interaction with surroundings (e.g., in composites)


ensembles (films, fibers, forests)
individual CNTs
mm²
Sample size
< μm²
low
high
Measurement resolution

Typical CNT film Raman spectrum



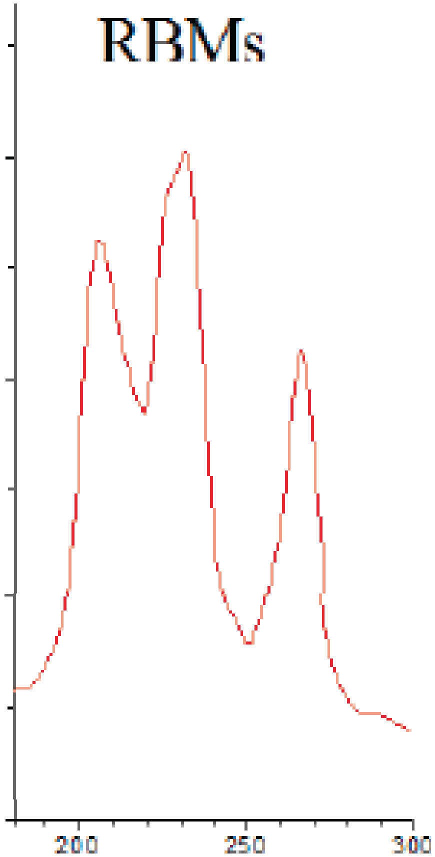
RBM =
SWNT diameter

G/D Ratio =
CNT quality

D-band = Defects in CNTs and defective carbon on substrate

lambdasolutions.com

after Jorio et al., New Journ. Phys., 5:139.1–139.17, 2003

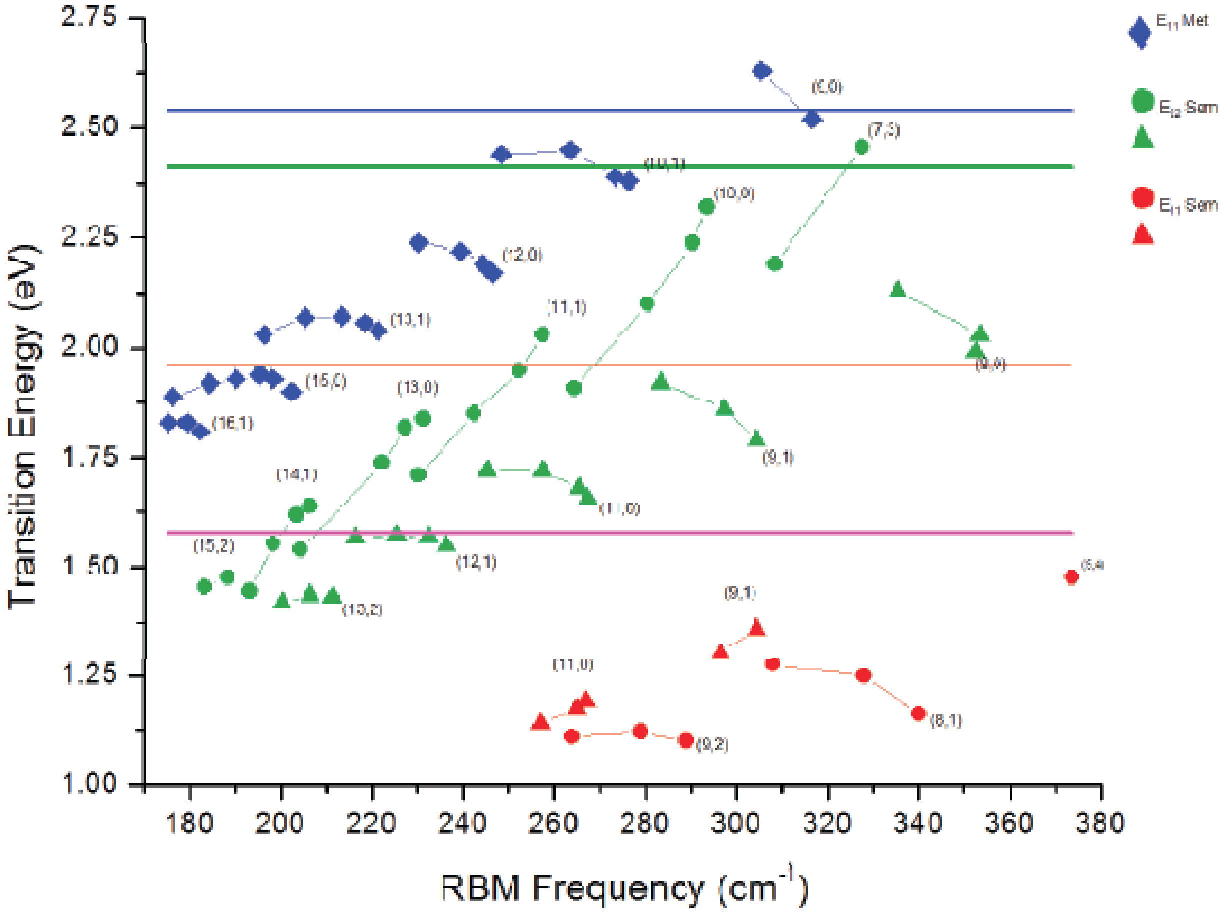


$$\omega \cong 220 / d + 10$$

$$d \cong \frac{220}{\omega - 10}$$

A. Swan, chapter 4 in "Measurement Issues in Single Wall Carbon Nanotubes", NIST 960-19

The Kataura plot: visibility vs. laser energy



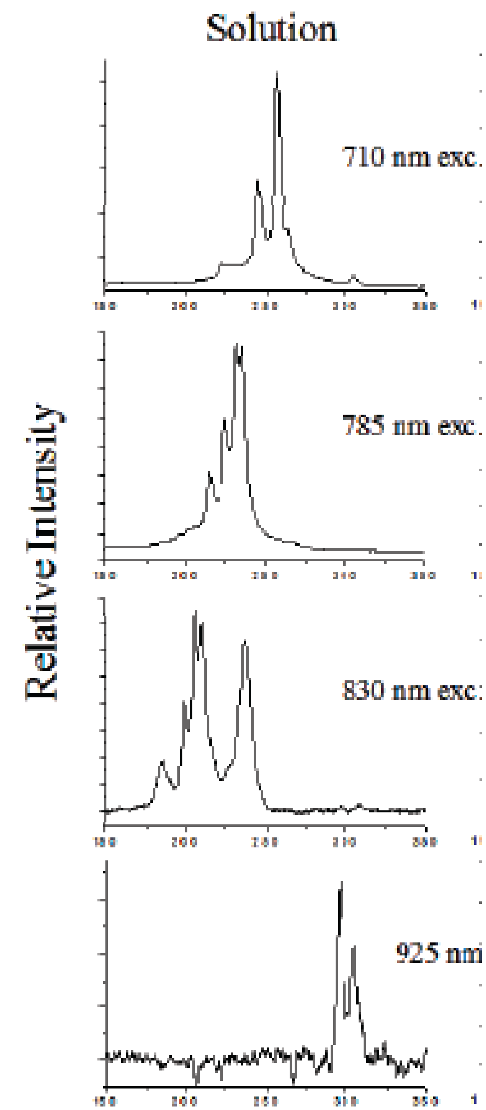
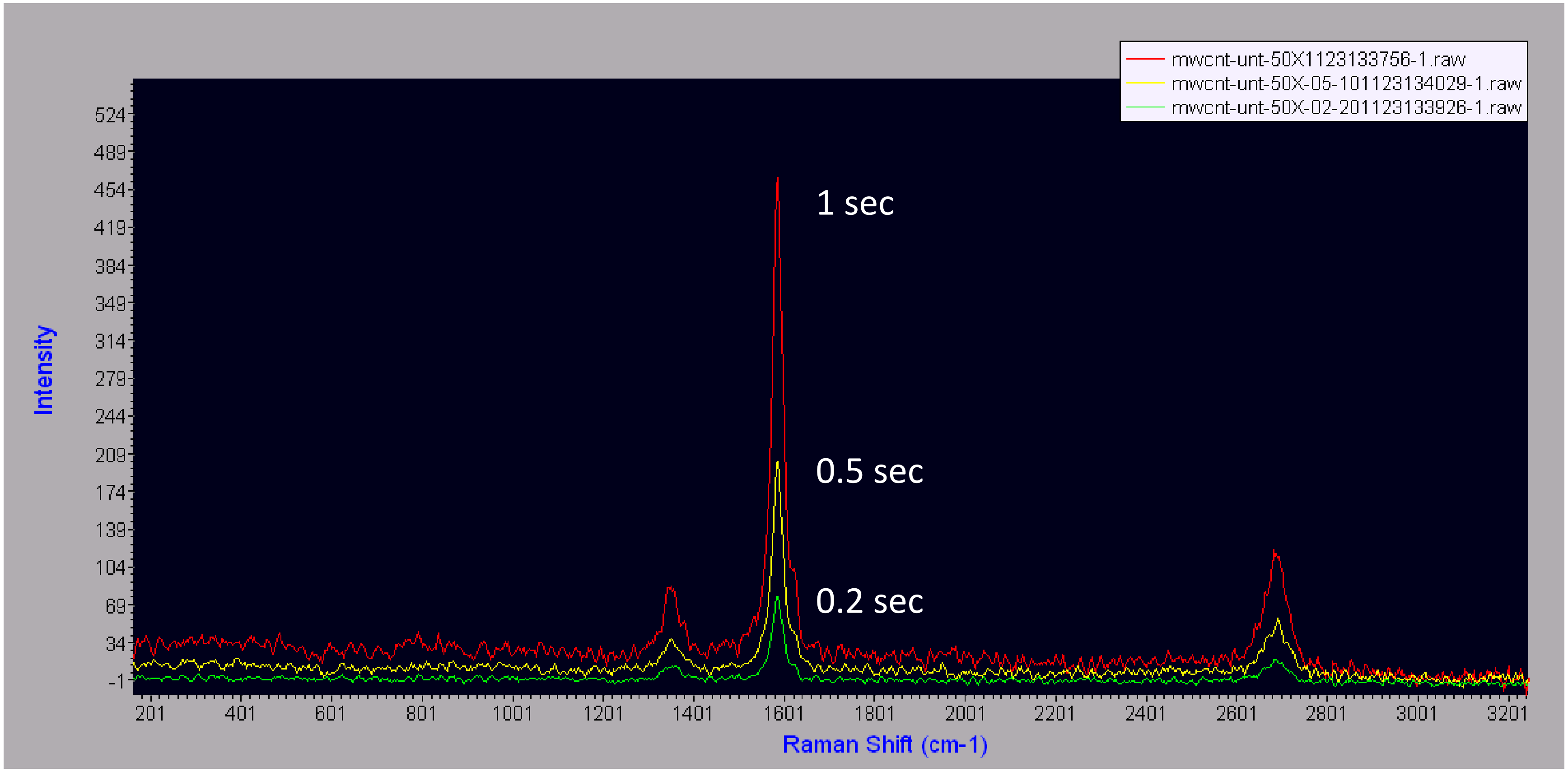


__Figure 4.3.__ Experimentally determined Kataura plot for SWNTs in sodium dodecyl sulfate (SDS) solution. The colored horizontal bars represent different common laser energies (blue: 488 nm, green: 514.5 nm, red: 632.8 nm, magenta: 785 nm). Data points are grouped according to common 2n+m = constant families, with the near zig-zag terminus of each family identified. For semiconducting tube types, circles represent chiralities with mod (n-m, 3) = -1, while triangles represent chiralities with mod (n-m, 3) = +1. Experimental data obtained from (11-14).

A. Swan, chapter 4 in “Measurement Issues in Single Wall Carbon Nanotubes”, NIST 960-19

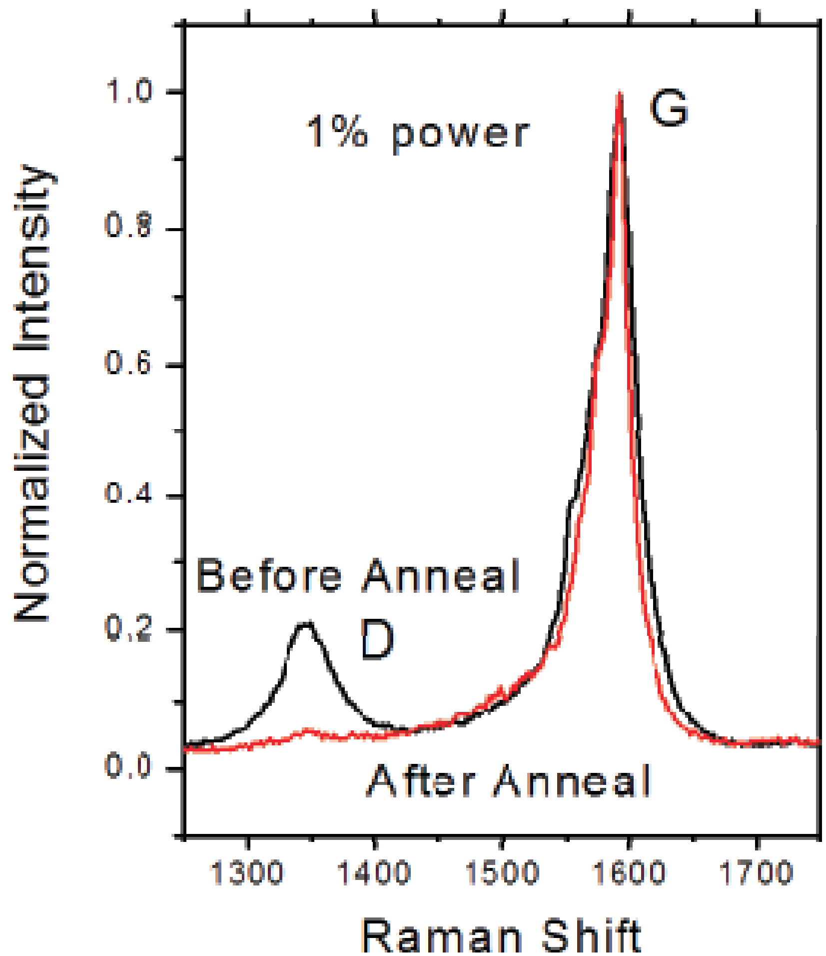
MWNT spectra – effect of collection time



→ Improvements in detectors, control of laser power

courtesy of Victor Sapirstein, Lambda Solutions Inc.

G/D ratio as a measure of quality

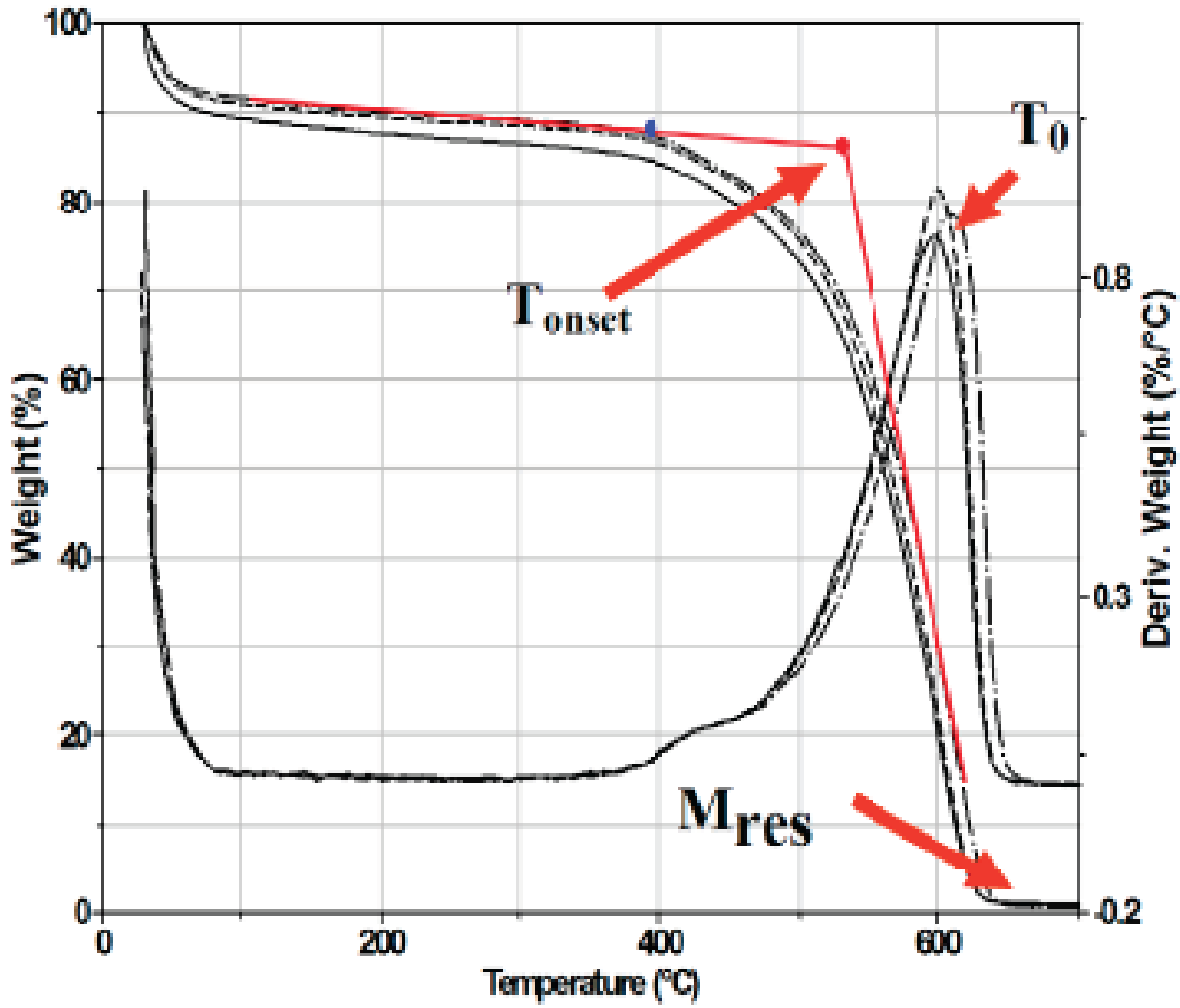


Example: Annealing of a DWNT powder reduces G-band peak intensity and width

- High-quality samples: G/D = 10-100

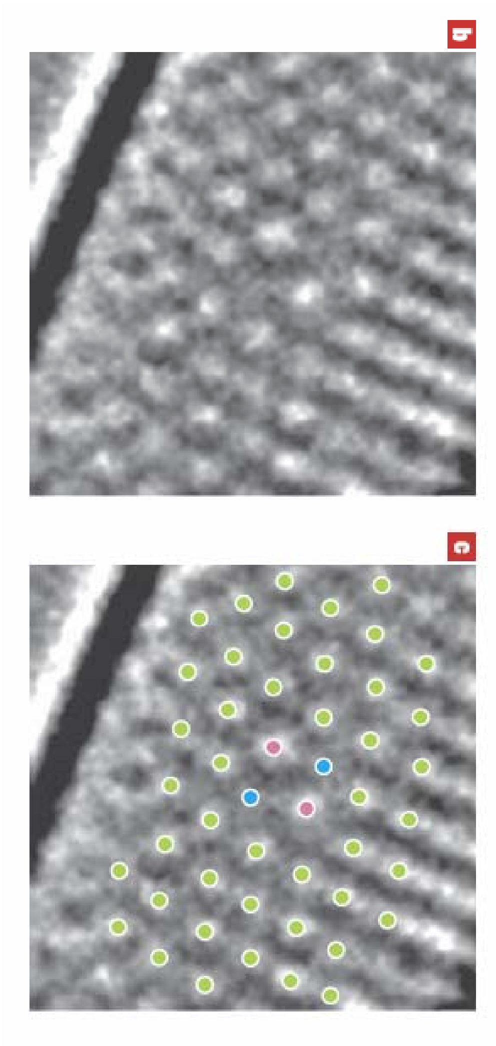
A. Swan, chapter 4 in “Measurement Issues in Single Wall Carbon Nanotubes”, NIST 960-19

Measuring purity by thermogravimetric analysis (TGA)



S. Arepalli, chapter 2 in "Measurement Issues in Single Wall Carbon Nanotubes", NIST 960-19

Identification of defects in TEM



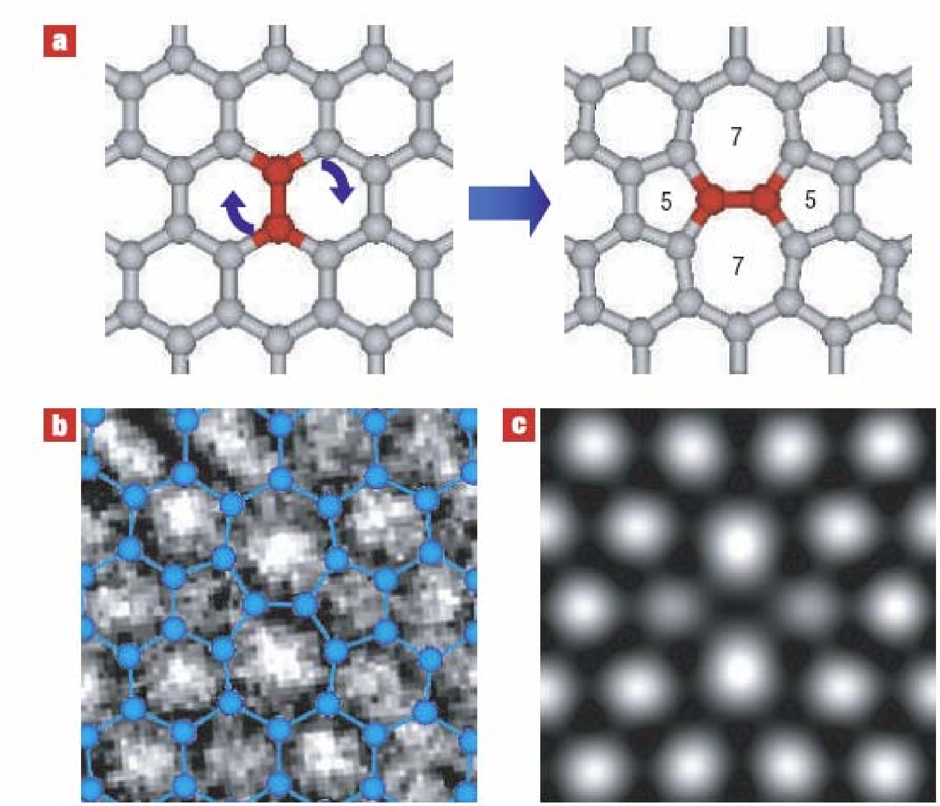
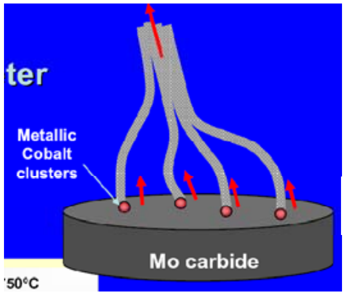


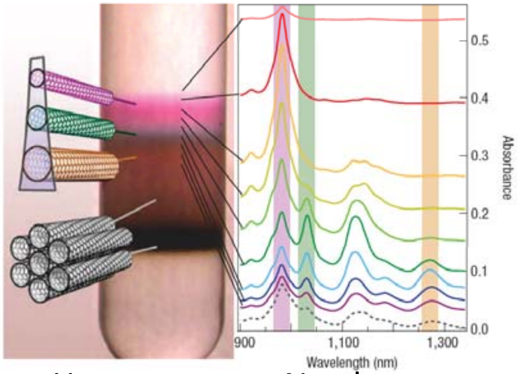
Figure 2 Atomic arrangement of the Stone–Wales (SW) model. a, The SW transformation leading to the 5–7–7–5 defect, generated by rotating a C–C bond in a hexagonal network. **b**, HR-TEM image obtained for the atomic arrangement of the SW model. **c**, Simulated HR-TEM image for the model shown in **b**.

Growth/processing advances help metrology

- Precise control of catalyst size and composition
  - Growth of narrow chirality distributions
- CNT separations by diameter, chirality, and length
  - Ultracentrifugation
  - Gel electrophoresis
  - DNA wrapping/functionalization
- Directed placement of CNTs on substrates
  - Aligned (vertical, horizontal) growth
  - Dielectrophoresis
- Understanding of how dispersion methods modify CNT quality, bundling, length

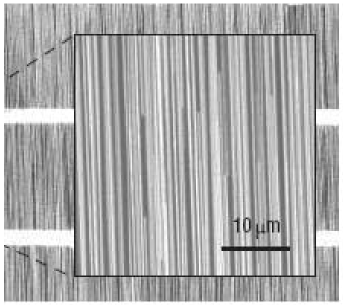


Resasco, SWeNT



Hersam group, Northwestern

Rogers group, UIUC



Challenges in overcoming CNT growth limits

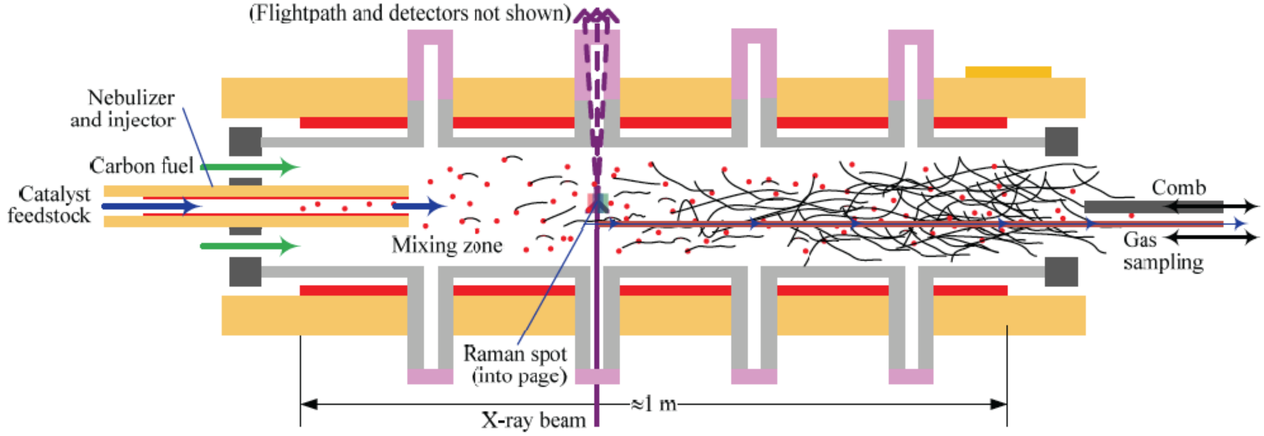
- How is carbon incorporated into growing CNTs?
- What determines CNT chirality?
  - When is it established?
  - What causes chirality changes?
- What limits CNT growth rate and length?
- How do interactions among CNTs affect collective growth and assembly?

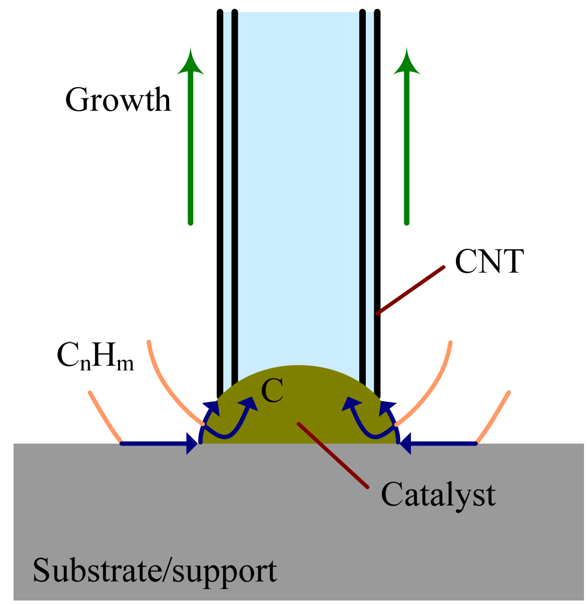
→Can CNTs be grown to indefinite length?

→What are the limits of alignment and density?

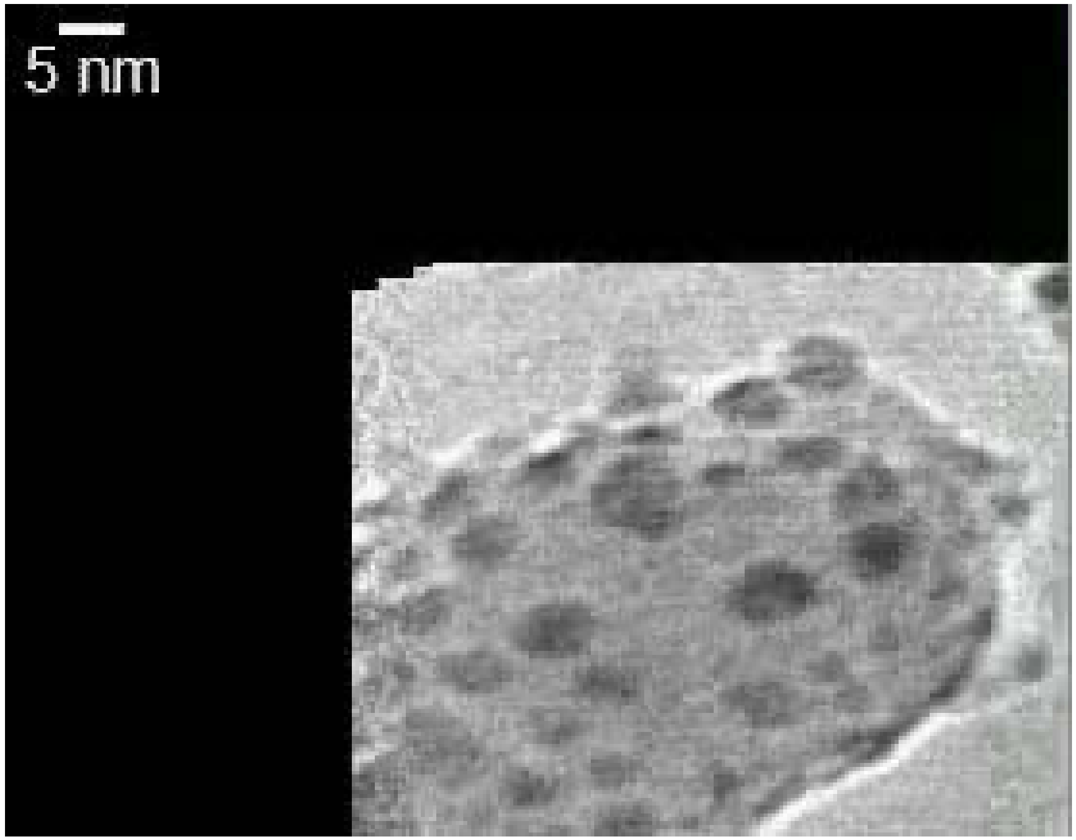
CNT process metrology

- Catalyst
  - Size (and distribution)
  - Chemical state
  - Composition
- Gas chemistry
  - Hydrocarbons
  - Hydrogen
  - Oxygen and water
- Temperatures and flows
- How the CNTs evolve *in situ*



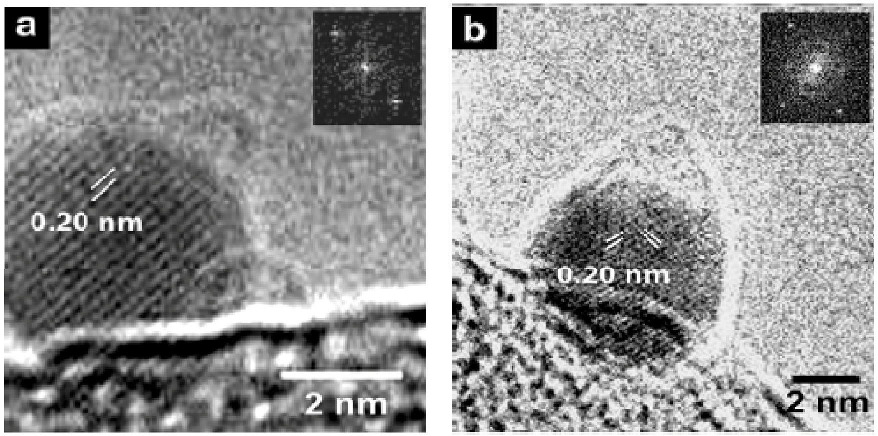


Watching SWNT nucleation in TEM



Hofmann, Sharma, et al. *Nano Letters* 7:602-608, 2007.

Watching SWNT nucleation in TEM



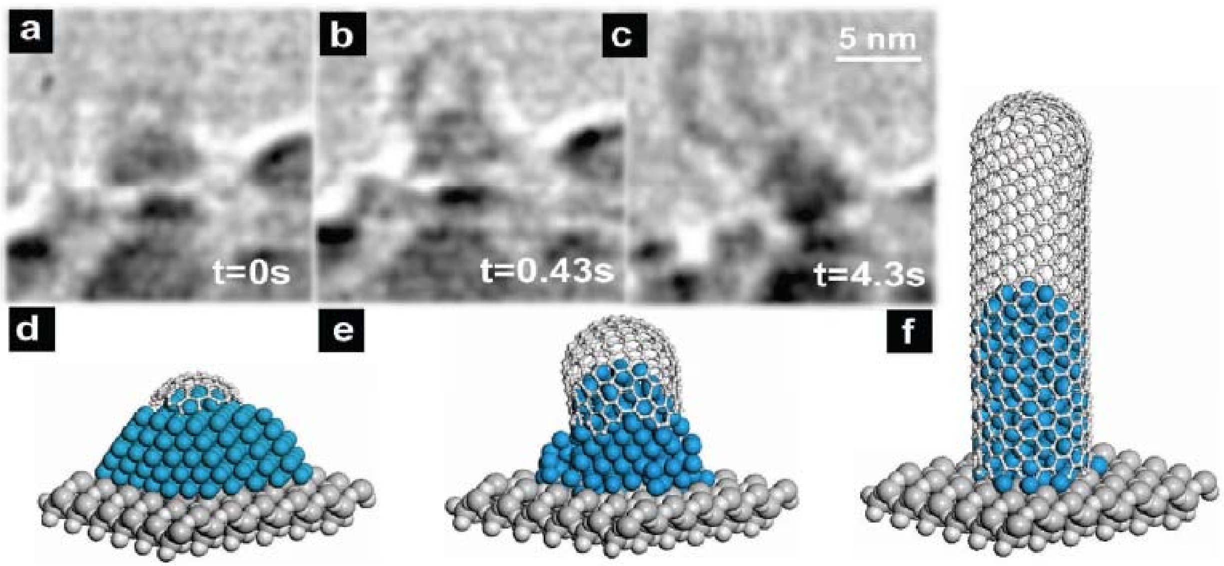
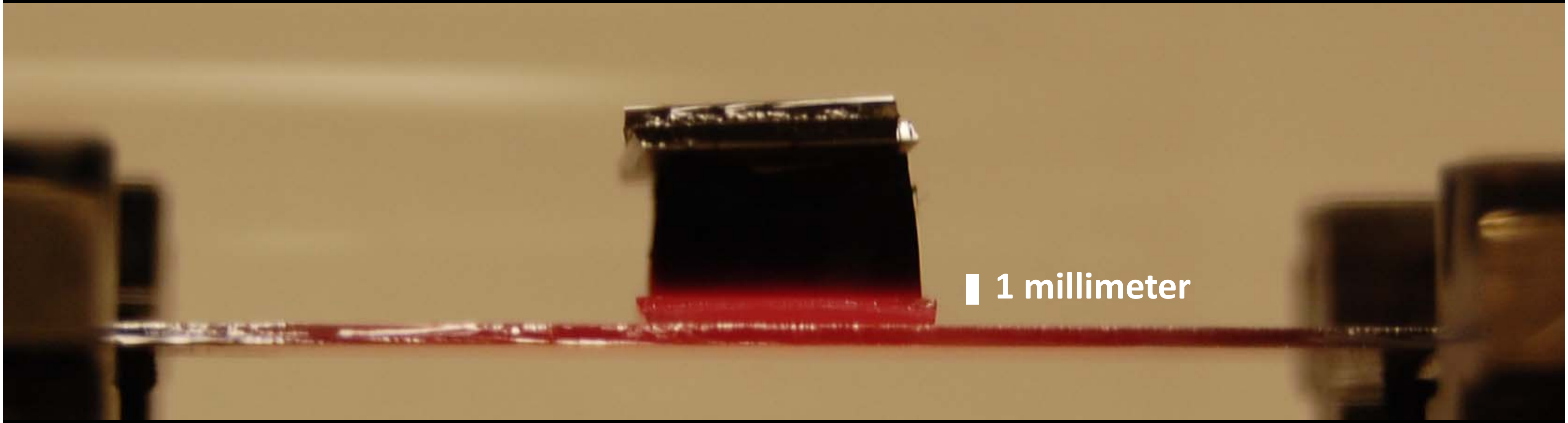


Figure 7. (a−c) ETEM image sequence of Ni-catalyzed CNT root growth recorded in 8×10^{-3} mbar C_2H_2 at 615 °C (extracted from Supporting Information video S2). The time of the respective stills is indicated. (d−f) Schematic ball-and-stick model of different SWNT growth stages.

Hofmann, Sharma, et al. *Nano Letters* 7:602-608, 2007.

Problem: CNT growth is a "black box"



Meshot, Plata, Tawfick, Zhang, Verploegen, Hart. *ACS Nano* 3(9):2477-2486, 2009.
Hart and Slocum, *J. Phys. Chem. B* 110:8250-7, 2006.
Hart, van Laake, Slocum, *Small* 3(5):772-777, 2007.

CNT forest: a model system to understand population dynamics during growth

1. Catalyst preparation and pre-treatment

- deposit thin film
- establish chemical state (e.g., $Fe_2O_3 \rightarrow Fe$)
- establish particle size

2. Nucleation

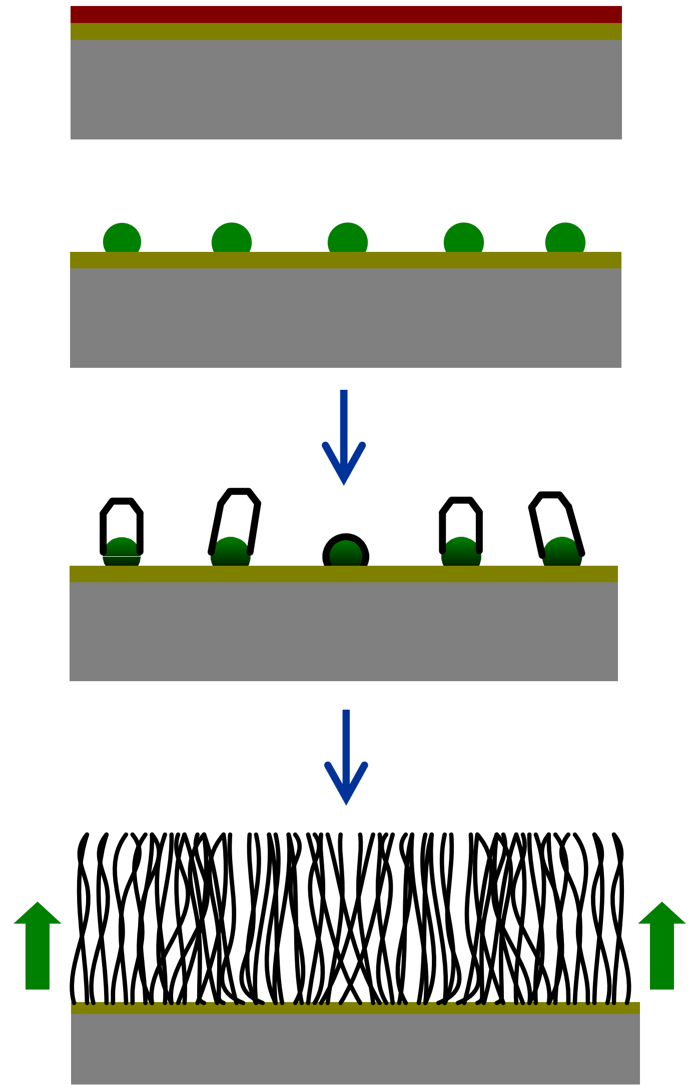
- create cap and determine CNT structure
- maximize yield and uniformity

3. Growth

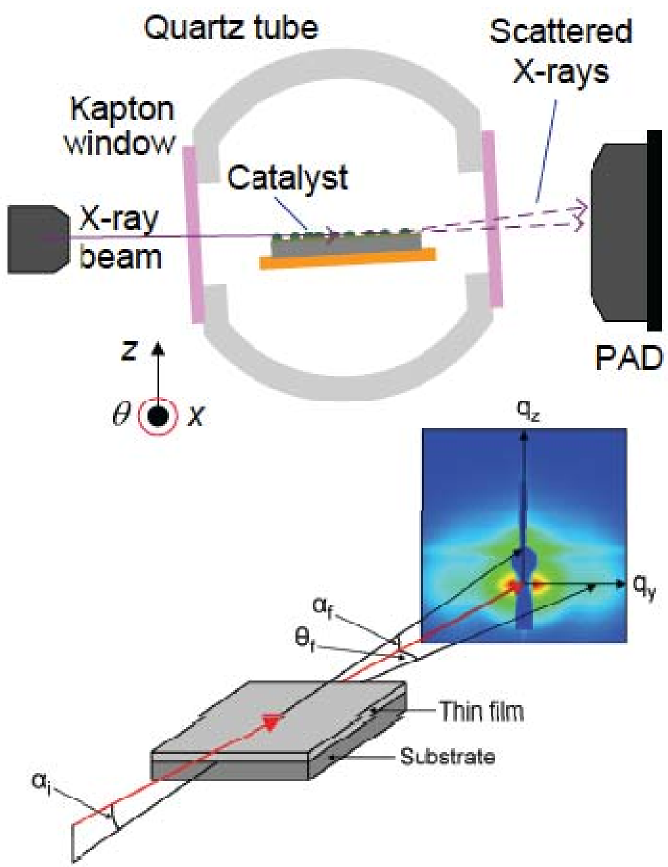
- control carbon “construction”
- maintain uniformity (diameter, density)

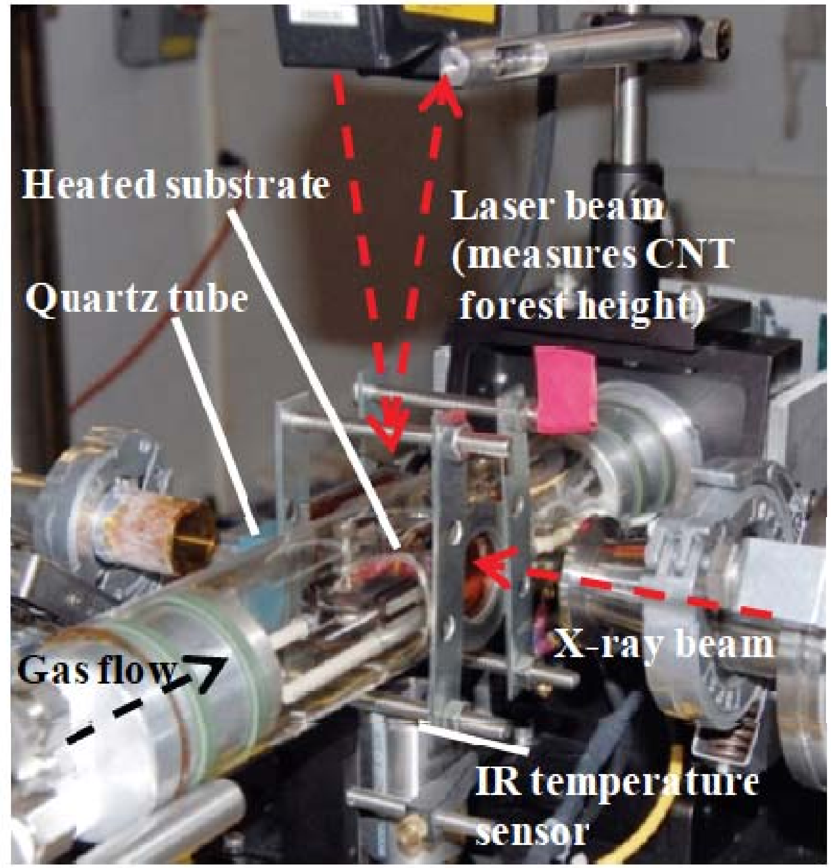
4. Termination

- maximum height = 1-20 mm ***…why?***



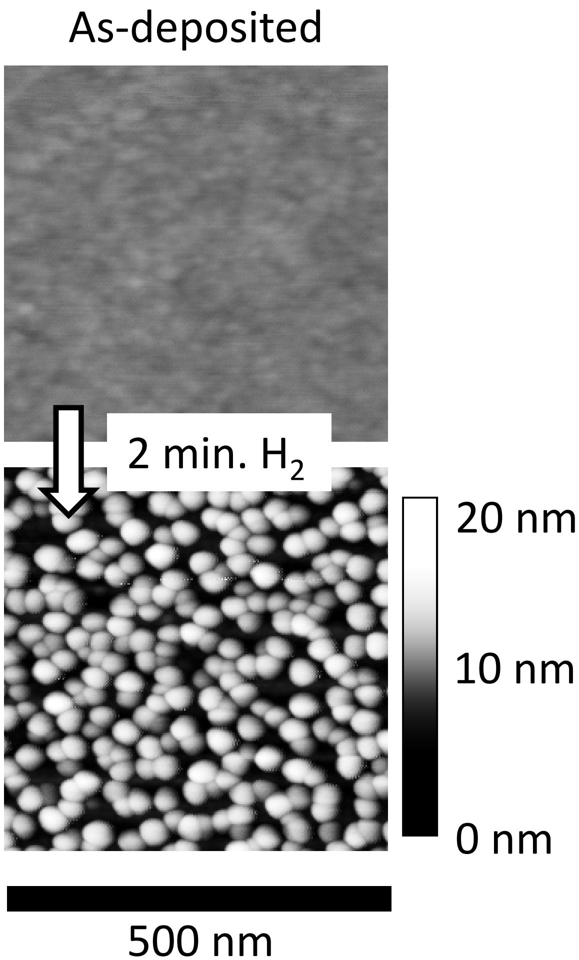
In situ X-ray scattering of CNT film growth

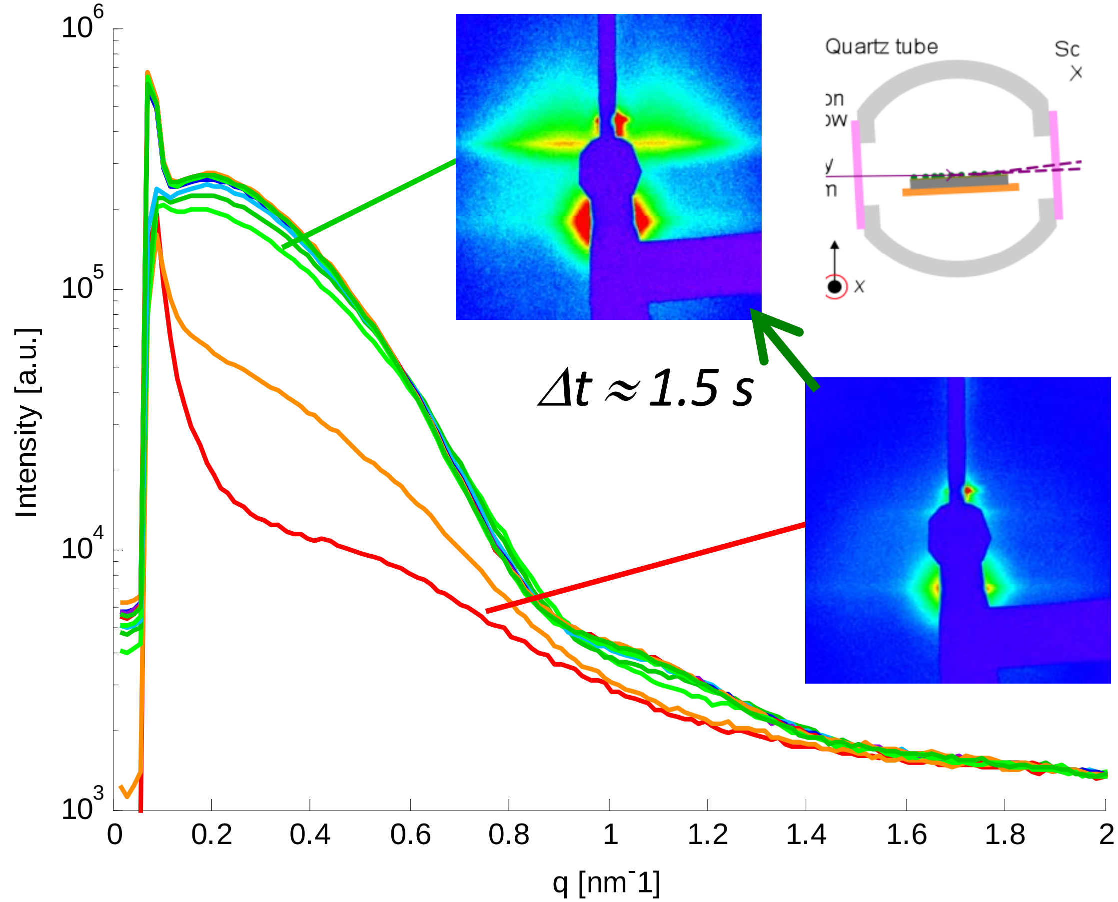




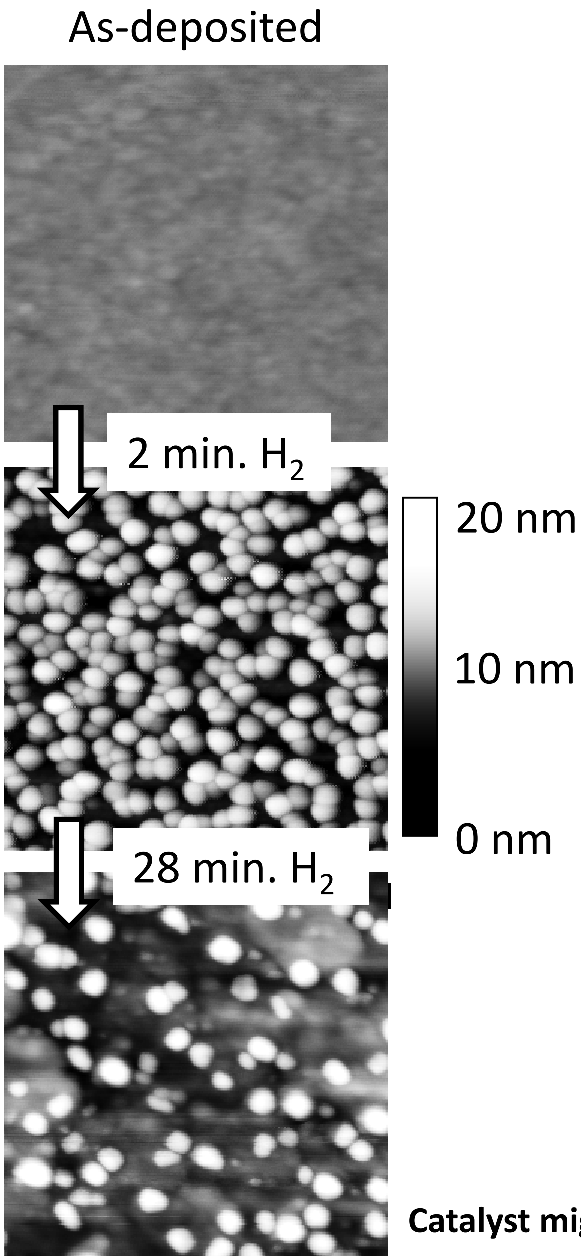
G1 beamline at Cornell High Energy Synchrotron Source

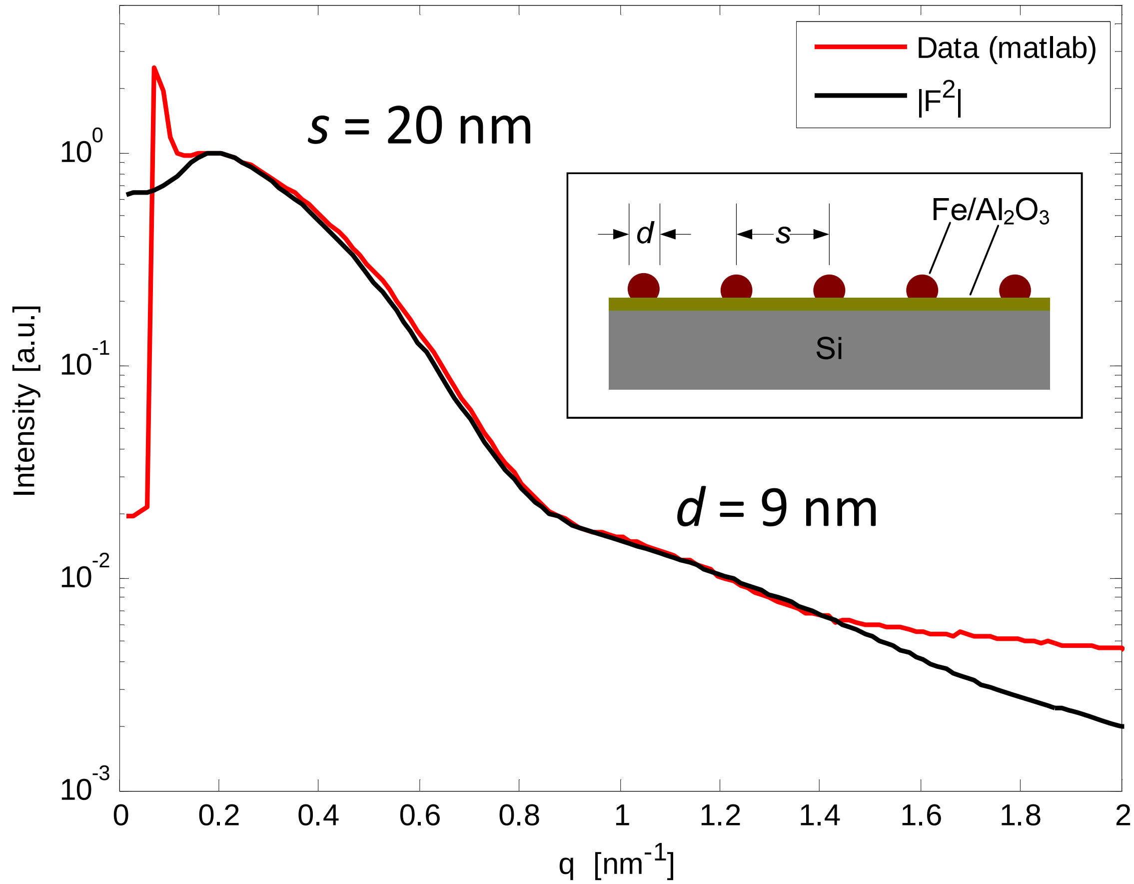
Catalyst particles form rapidly on the substrate





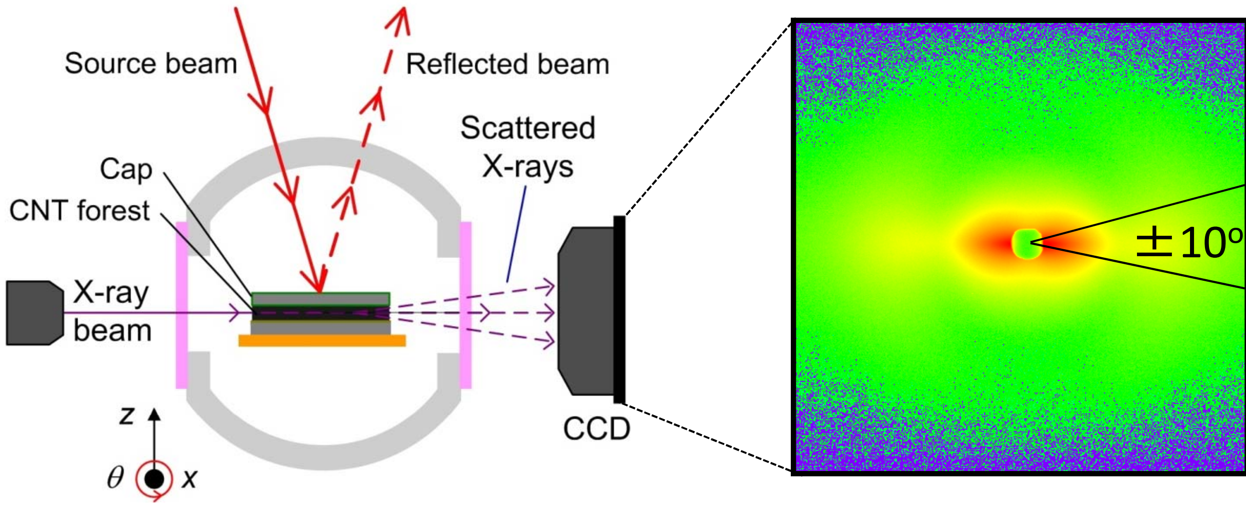
Fe agglomerates rapidly yet coarsens slowly





Catalyst migration → Kim et al., J. Phys. Chem. Lett, 2010.

Measuring CNT diameter distribution by SAXS

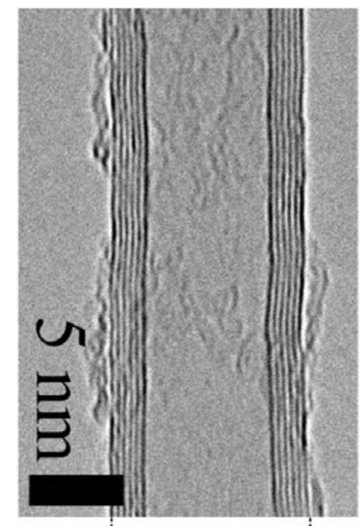


$$\rightarrow \int_{-\pi/18}^{\pi/18} I(q,\phi)\,d\phi$$

$$I_C(q) = \frac{\int_0^\infty P(R) f^2(q,R)\,dR}{\int_0^\infty P(R)\,dR}$$

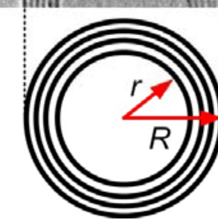
$$P(R) = \frac{1}{R\sigma\sqrt{2\pi}} \exp\left[\frac{-(\ln R - \mu)^2}{2\sigma^2}\right]$$

Log-normal **distribution of core-shell cylinders**



$$f(q,R,c) = \Delta\rho R \frac{2[J_1(Rq) - cJ_1(cRq)]}{qR(1 - c^2)}$$

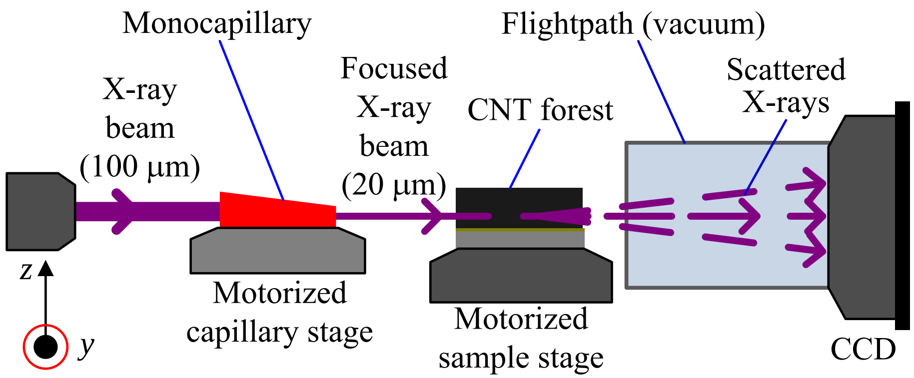
$c = r/R$

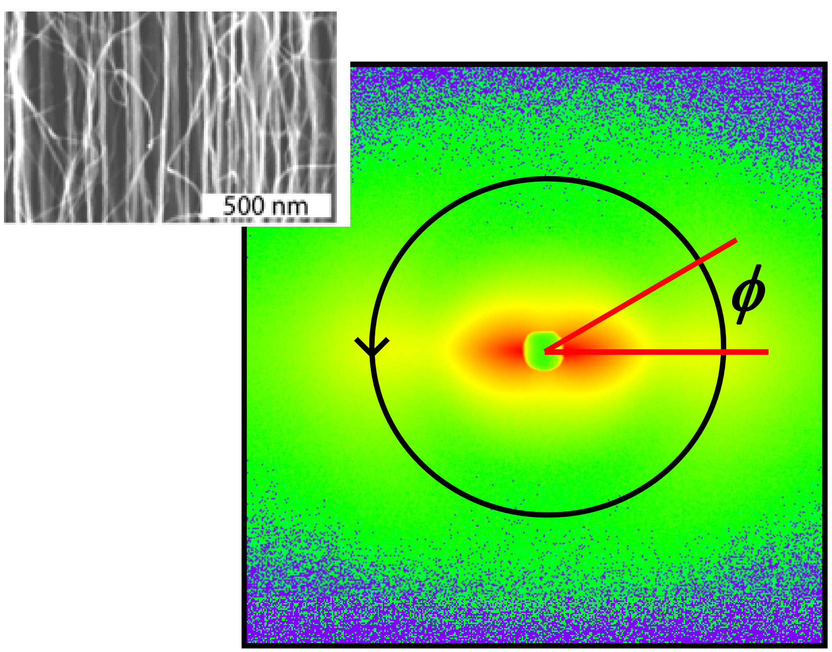


Wang, Bennett, Verploegen, Hart, Cohen, *J. Phys. Chem. C* 111(16):5859-5865, 2007.
Meshot, Plata, Tawfick, Zhang, Verploegen, Hart. *ACS Nano,* 3(9):2477-2486, 2009.

Quantifying CNT alignment

Transmission SAXS





Hermans orientation parameter

$$H = \frac{1}{2}\left(3\left\langle \cos^2 \phi \right\rangle - 1\right)$$

$$\left\langle \cos^2 \phi \right\rangle = \frac{\int_0^{\pi/2} I(\phi)\sin\phi \cos^2 \phi d\phi}{\int_0^{\pi/2} I(\phi)\sin\phi d\phi}$$

***H* = 1.0: perfect vertical**

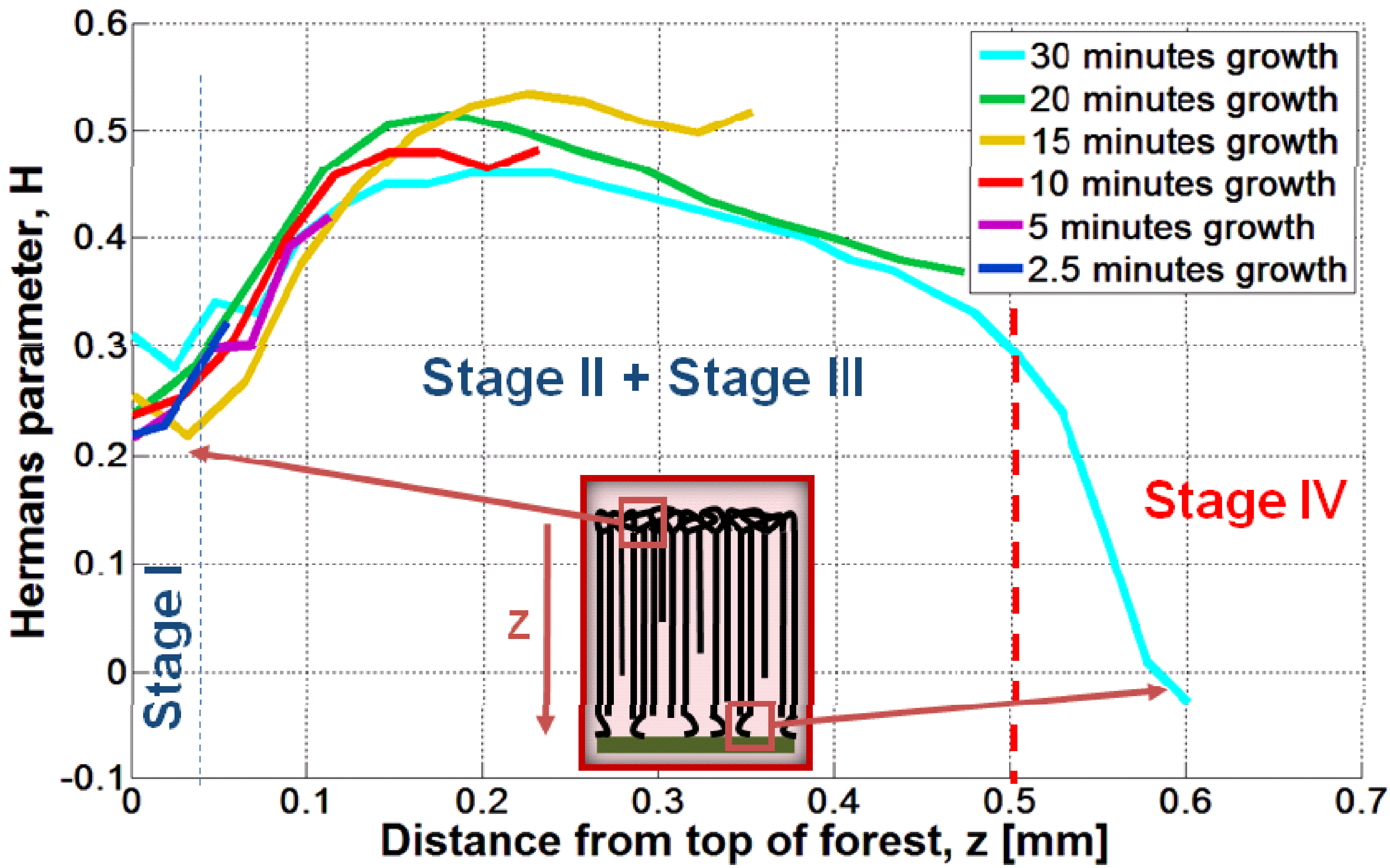
***H* = 0.0: random**

***H* = -0.5: horizontal**

Hermans, 1948.

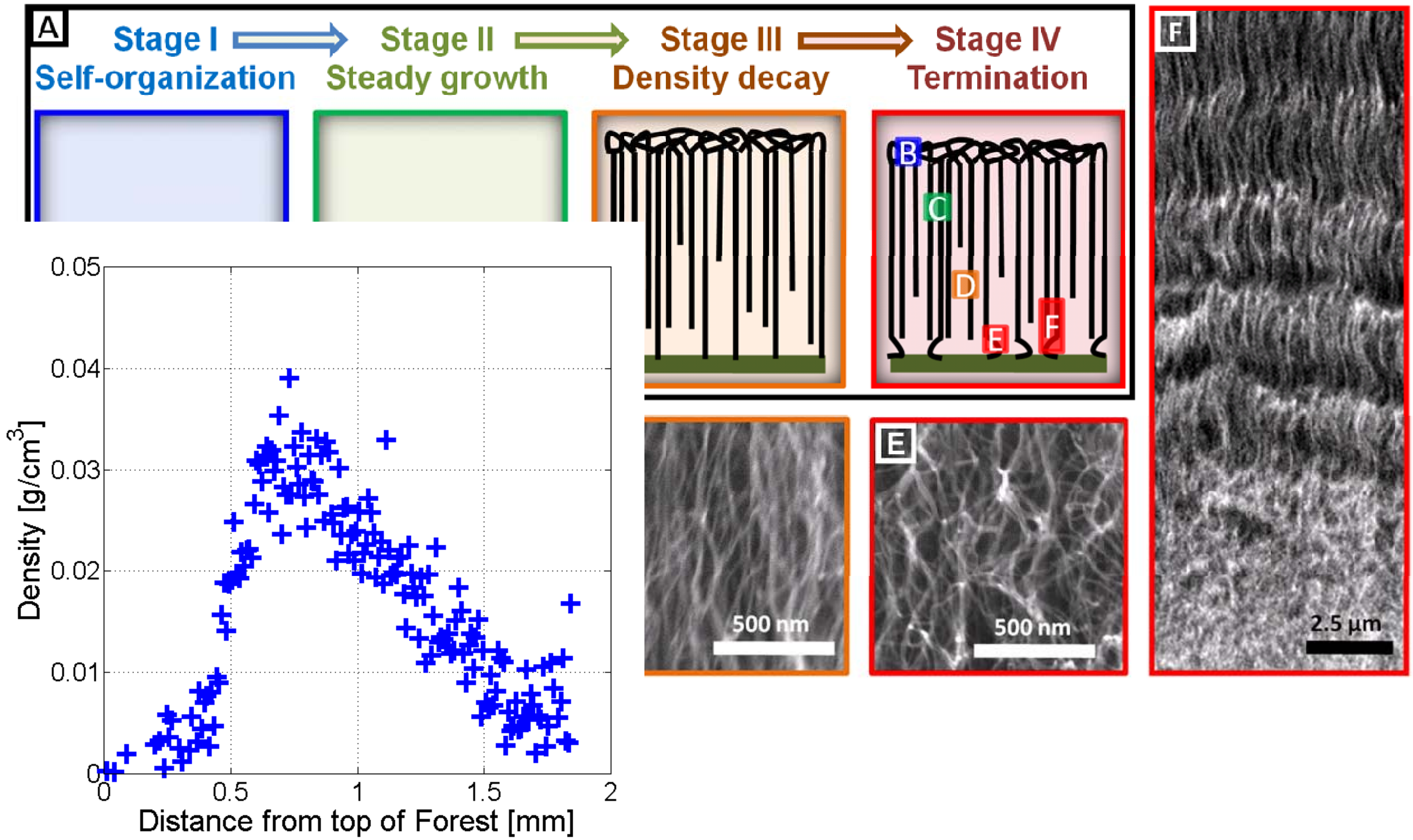
Wang, Bennett, Verploegen, Hart, Cohen, *J. Phys. Chem. C* 111(16):5859-5865, 2007.

Time evolution of alignment



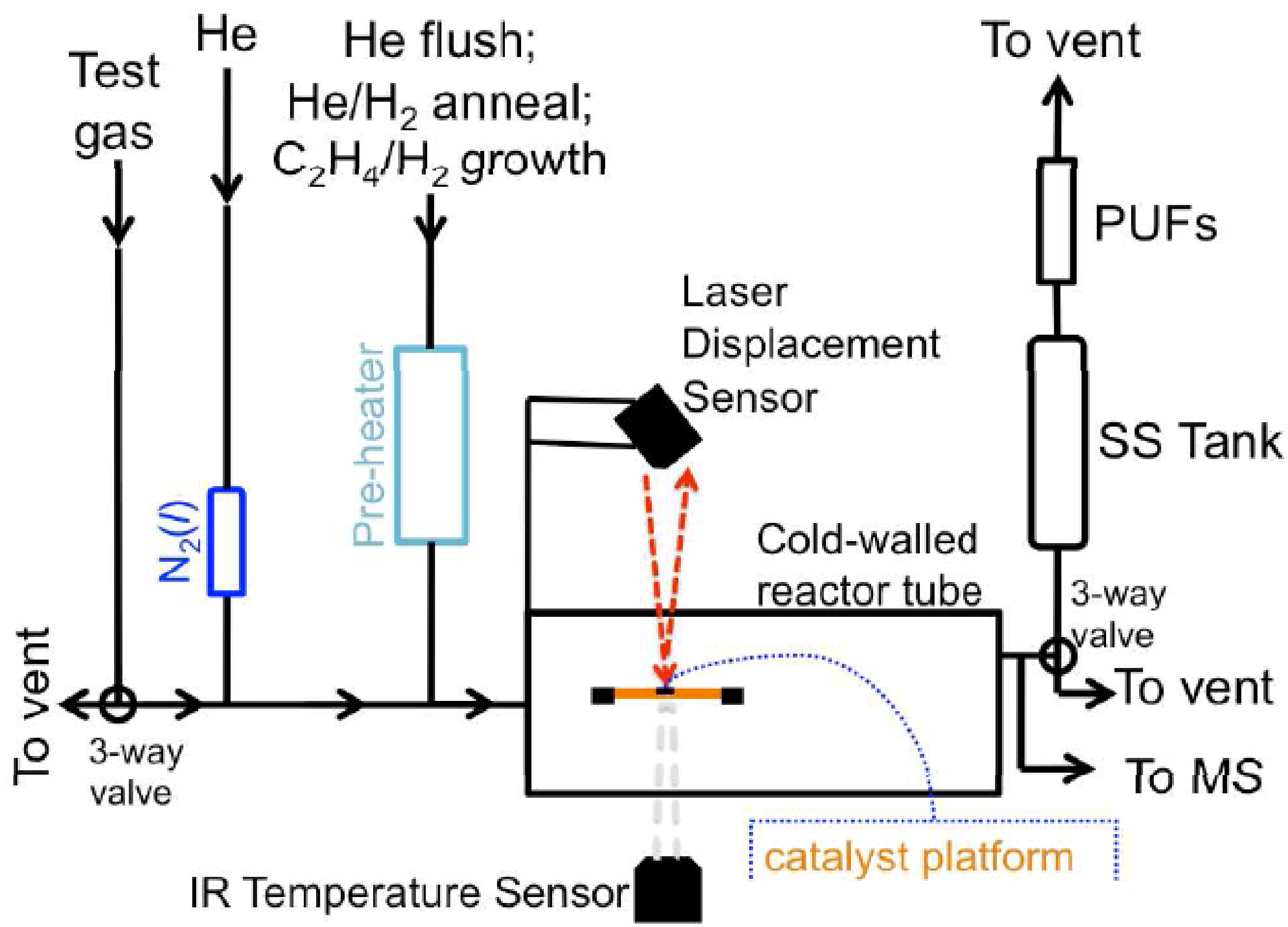
Bedewy, Meshot, Guo, Lu, Hart. *J. Phys. Chem. C*, 113:20576-20582 2009.

Collective growth model

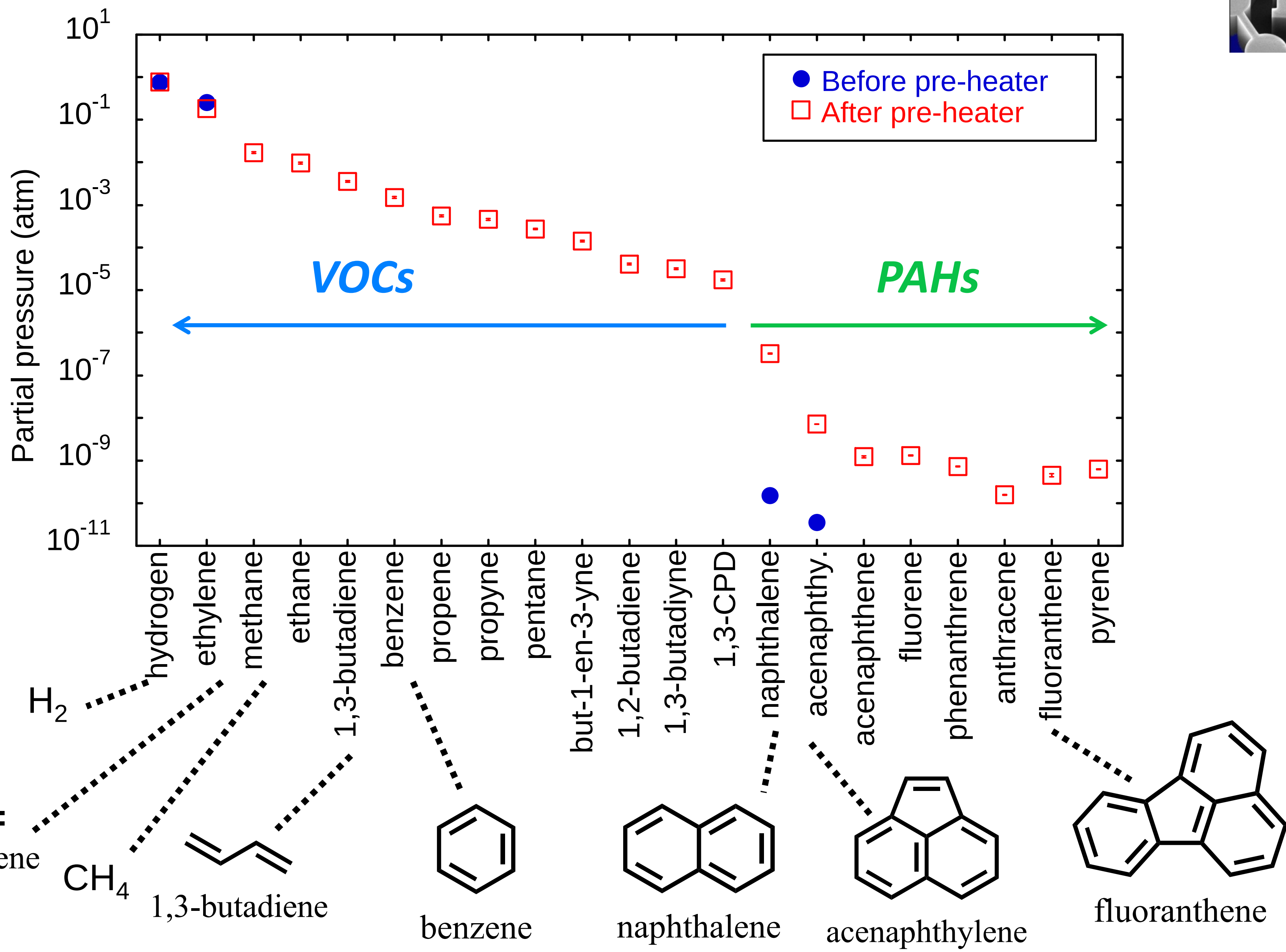


Bedewy et al. *J. Phys. Chem. C* 113:20576-20582, 2009.

Metrology of the reactor environment

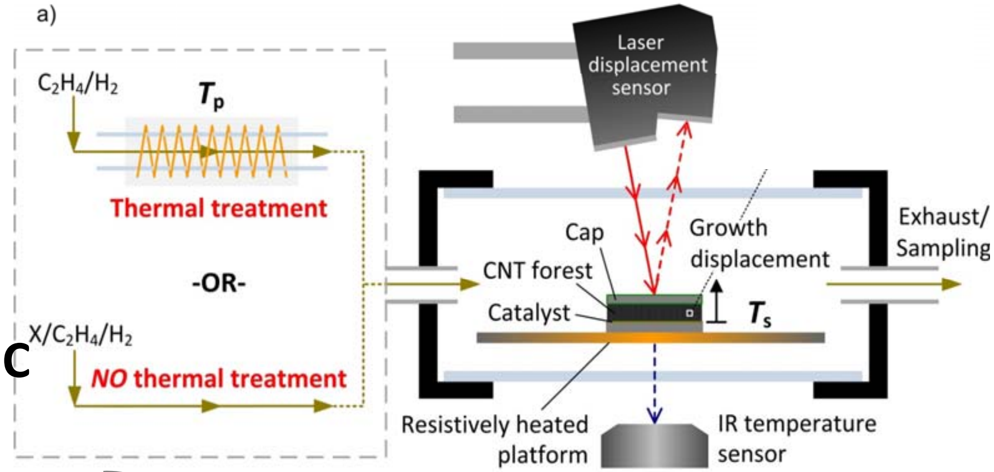


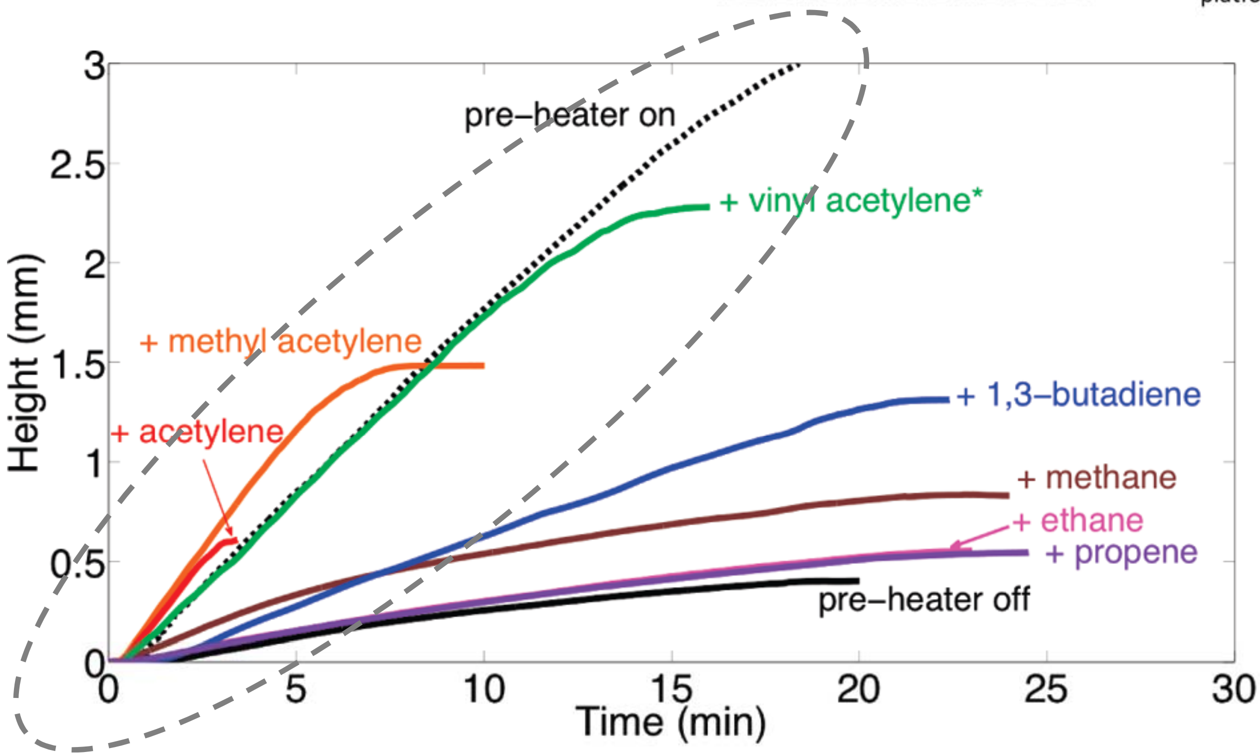
Plata, Meshot, et al. *ACS Nano* 4(10):7185-7192, 2010.


Partial pressure (atm)
10^1
10^-1
10^-3
10^-5
10^-7
10^-9
10^-11
Before pre-heater
After pre-heater
VOCs
PAHs
hydrogen
ethylene
methane
ethane
1,3-butadiene
benzene
propene
propyne
pentane
but-1-en-3-yne
1,2-butadiene
1,3-butadiyne
1,3-CPD
naphthalene
acenaphthy.
acenaphthene
fluorene
phenanthrene
anthracene
fluoranthene
pyrene
H2
ethylene
CH4
1,3-butadiene
benzene
naphthalene
acenaphthylene
fluoranthene

Selective testing reveals *alkynes* as effective precursors

All T_s = 750 ° C, T_p = 25 ° C
(+ 0.01 atm of select HC)





Diameter remains constant

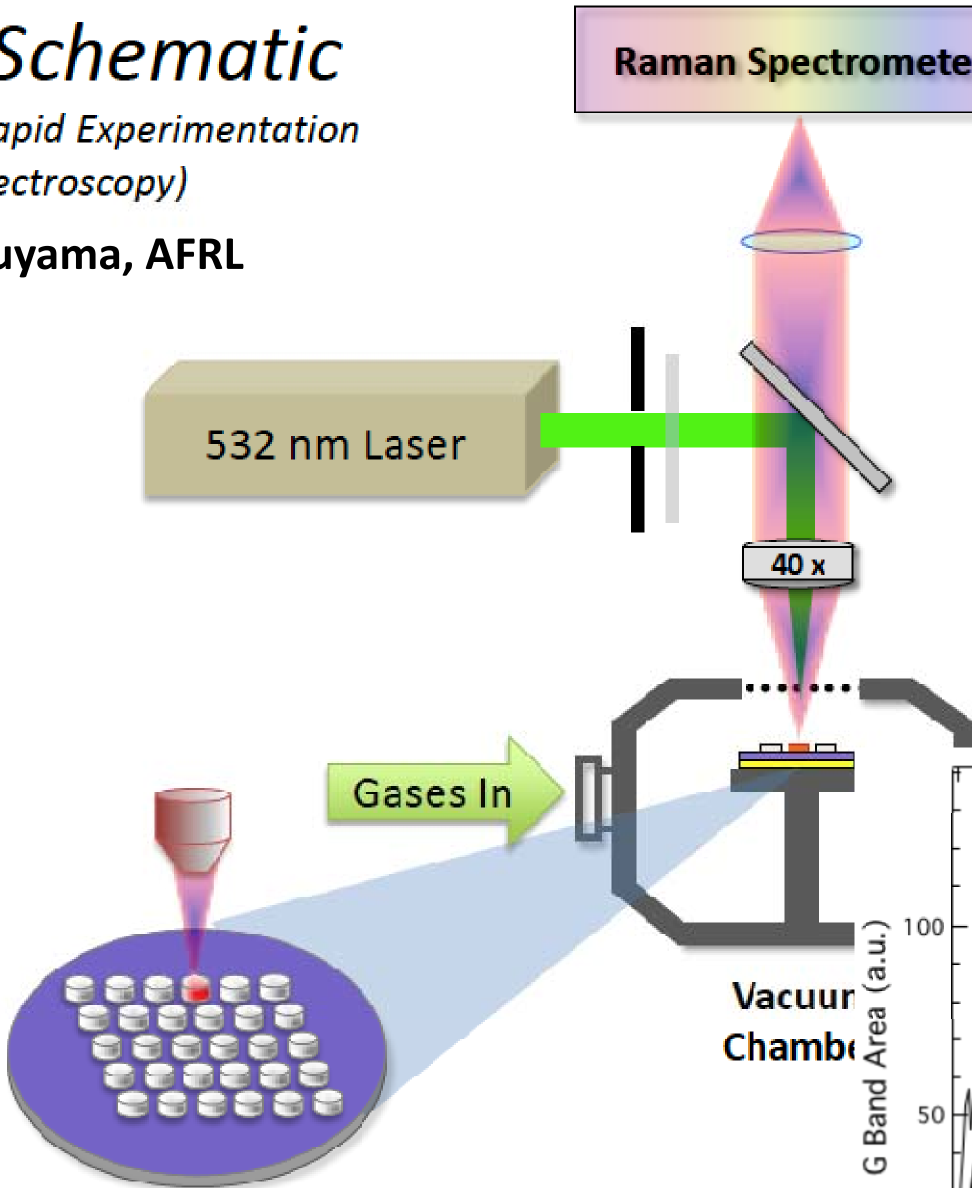
	CNT diameter [nm]
pre-heater ON	**10.0**
+acetylene	**10.2**

Plata, Meshot, et al. *ACS Nano* 4(10):7185-7192, 2010.

ARES Schematic

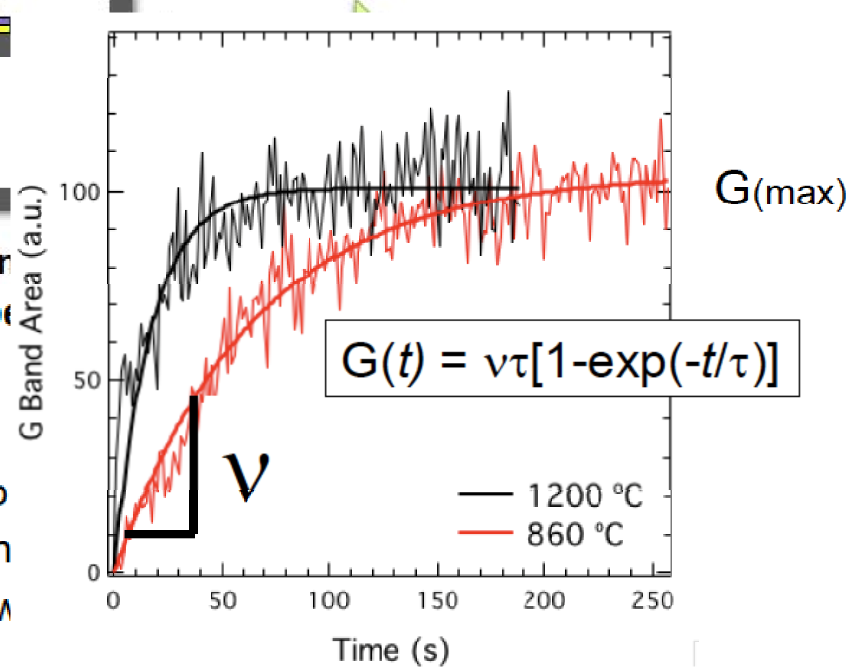
(Adaptive Rapid Experimentation & in-situ Spectroscopy)

Benji Maruyama, AFRL



CVD Parameters

- Chamber pressure 25 Torr
- Sputtered 2 nm Fe and Ni
- $C_2H_4/Ar/H_2$: 5/25/10 sccm



- Grow carbo
- Collect Ram
- Obtain grow

Discussion topics

- Accelerating rapid quality control of CNT production
  - Minimum suite of methods?
  - What are the key metrics of process health?
  - What are the needs/uses of in situ techniques?
  - Ways to close the loop between growth process and material properties
- Demands for advancement in tools/techniques
  - Statistical analysis of CNT populations
  - Characterization across entire SWNT/DWNT diameter range
  - Compact instruments and dedicated systems for in situ measurements
- Where do the "growth limits" matter?
- Characterization standards/protocols for EHS qualification

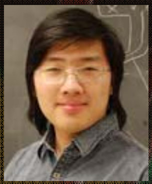

MUSE

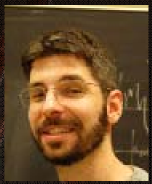
Mechanosynthesis Group


Eric Meshot


Mostafa Bedewy


Erik Polsen


Jinjing Li


Davor Copic


Sei Jin Park


Justin Beroz


Sameh Tawfick

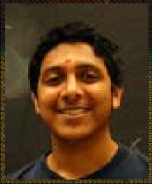

Michael De Volder

imec


Megan Roberts


Dan McNerny


Ryan Oliver

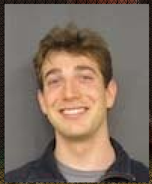

Anand Bharath

Precursor chemistry: Desiree Plata (Mt. Holyoke)

X-ray scattering at Cornell: Arthur Woll, Sol Gruner


Yongyi Zhang


Jong Ok


Aaron Schmidt


Anne Juggernauth

Michigan Engineering

LOCKHEED MARTIN

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