Carbon nanotube metrology for science and manufacturing

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

Configurations

- **individual**
  - Stanford, ETH

- **forest (aligned)**

- **yarn/sheet**
  - Nanocomp

- **network (tangled)**
  - Florida

- **dispersion**

Order =

- high
- low

Quantity =

- few
- many
Applications

Enabled by longer, more ordered CNTs

- Filtration/desalination
- 3D energy devices
- Thermal interfaces
- Lightweight conductors
- Organized composites

Interconnects
- Emissors, memory
- Transistors

Higher precision of CNT diameter (chirality) needed

Order
- high
- low

Quantity [#/vol]
- few (<< 1g)
- many

ESD/plastics
Batteries (powder electrodes)

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The 4th Carbon Nanotube Workshop at NIST: Control and Measurement of Chirality

September 23rd and 24th 2010
Hosted by the National Institute of Standards and Technology
Gaithersburg, MD 20899

Organizing Committee
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Measurement Issues in Single Wall Carbon Nanotubes

Edited by:
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NIST Materials Science and Engineering Laboratory

and
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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.

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

Sample size

< μm²

mm²

Measurement resolution

low

high

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Typical CNT film Raman spectrum

RBM = SWNT diameter

G/D Ratio = CNT quality

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

\[ \omega \approx \frac{220}{d} + 10 \]

\[ d \approx \frac{220}{\omega - 10} \]
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 $2n+m = \text{constant}$ families, with the near zigzag terminus of each family identified. For semiconducting tube types, circles represent chiralities with $\text{mod } (n-m, 3) = -1$, while triangles represent chiralities with $\text{mod } (n-m, 3) = +1$. 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)
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/functionlization

- Directed placement of CNTs on substrates
  - Aligned (vertical, horizontal) growth
  - Dielectrophoresis

- Understanding of how dispersion methods modify CNT quality, bundling, length
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
Watching SWNT nucleation in TEM

Figure 7. (a–c) ETEM image sequence of Ni-catalyzed CNT root growth recorded in $8 \times 10^{-3}$ mbar $\text{C}_2\text{H}_2$ 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.

Problem: CNT growth is a “black box”

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$_2$O$_3$ $\rightarrow$ 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
Catalyst particles form rapidly on the substrate

As-deposited

2 min. H₂

Δt ≈ 1.5 s
Fe agglomerates rapidly yet coarsens slowly

As-deposited

2 min. H₂

28 min. H₂

Measuring CNT diameter distribution by SAXS

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

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

Log-normal distribution of core-shell cylinders

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

\[ c = \frac{r}{R} \]

Quantifying CNT alignment

Transmission SAXS

Hermans orientation parameter

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

\[
\langle \cos^2 \phi \rangle = \frac{\int_0^{\pi/2} I(\phi) \sin \phi \cos^2 \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi}
\]

- \( H = 1.0 \): perfect vertical
- \( H = 0.0 \): random
- \( H = -0.5 \): horizontal

Hermans, 1948.
Time evolution of alignment
Collective growth model

Metrology of the reactor environment

Before pre-heater

After pre-heater

**VOCs**

**PAHs**

- Hydrogen
- Ethylene
- Methane
- Ethane
- Benzene
- Propene
- Propyne
- Pentane
- But-1-en-3-yne
- 1,2-butadiene
- 1,3-butadiyne
- 1,3-CPD
- Naphthalene
- Acenaphthylene
- Acenaphthene
- Fluorene
- Phenanthrene
- Anthracene
- Fluoranthene

- Ethylene
- Methane
- Ethane
- Benzene
- Propene
- Propyne
- Pentane
- But-1-en-3-yne
- 1,2-butadiene
- 1,3-butadiyne
- 1,3-CPD
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- Fluorene
- Phenanthrene
- Anthracene
- Fluoranthene

Selective testing reveals *alkynes* as effective precursors.

All $T_s = 750 \, ^\circ C$, $T_p = 25 \, ^\circ C$ (+ 0.01 atm of select HC)

ARCS 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

$G(t) = v\tau[1-\exp(-t/\tau)]$

Graph:
- $G_{\text{max}}$
- $G(t)$ for 1200 °C and 860 °C

Silicon Wafer
- Grow carb
- 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
Mechanosynthesis Group

Precursor chemistry: Desiree Plata (Mt. Holyoke)
X-ray scattering at Cornell: Arthur Woll, Sol Gruner