Carbon Nanotube Reference Materials and Characterization

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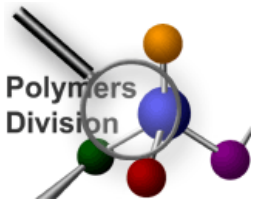
Gaithersburg, MD



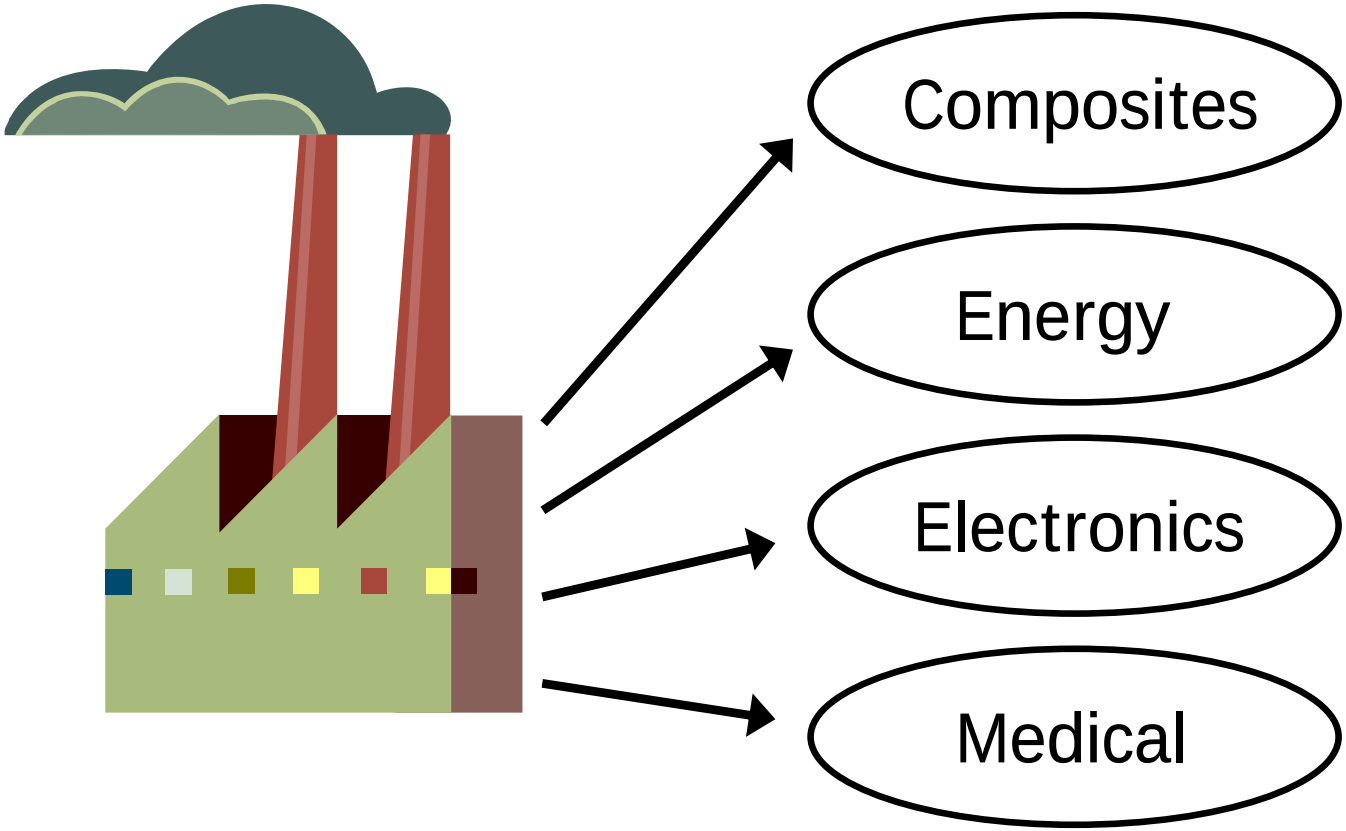
Nanotube Market

NANOTUBES Markets are expected to grow significantly

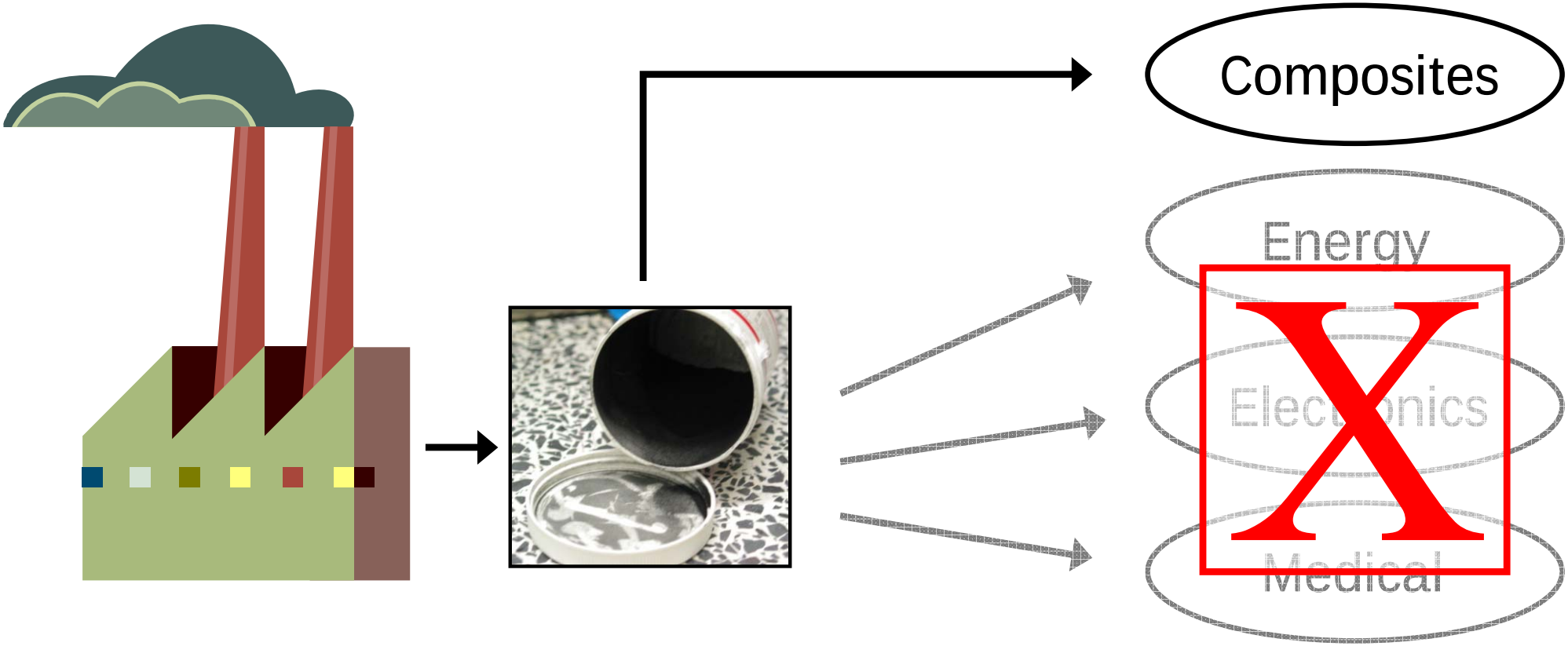
$ MILLIONS	2004	2009	2014
TOTAL DEMAND	$6	$215	$1,070
BY TYPE			
Single-walled nano-tubes	0	95	600
Multiwalled nano-tubes	6	120	470
BY END USE			
Electronics	0	90	395
Automotive	1	31	165
Aerospace/Defense	0	10	65
Other	5	84	445
BY REGION			
U.S.	2	57	290
Western Europe	1	32	180
Asia/Pacific	3	113	500
Other	0	13	100

SOURCE: Freedonia Group

Chemical & Engineering News
Carbon Nanotubes By The Metric Ton
November 12, 2007, Volume 85 (46), pp. 29-35

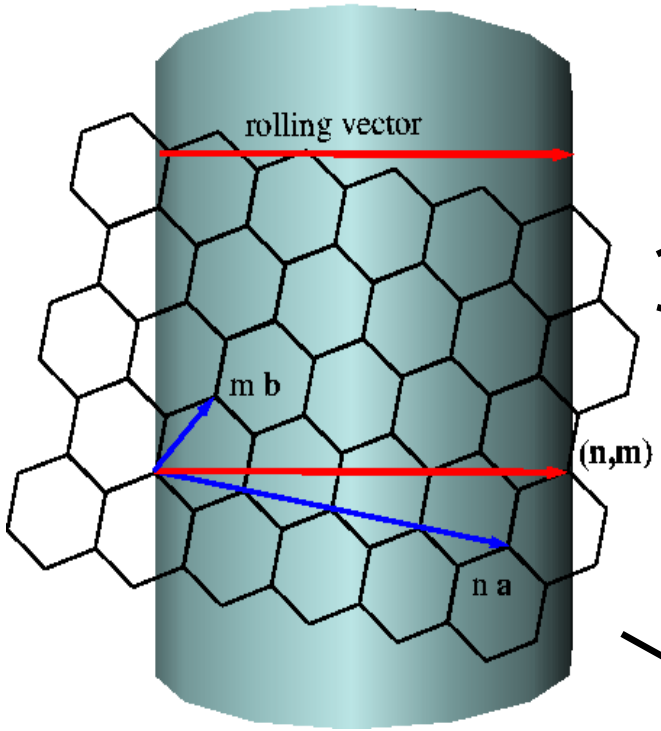


Market Problem

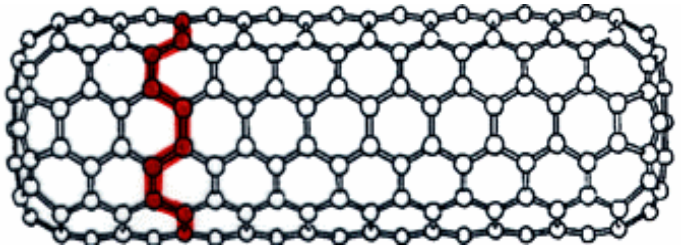


- Lack of purified materials for general audience.
- Many comparables – no common samples
- NanoEHS uncertainties

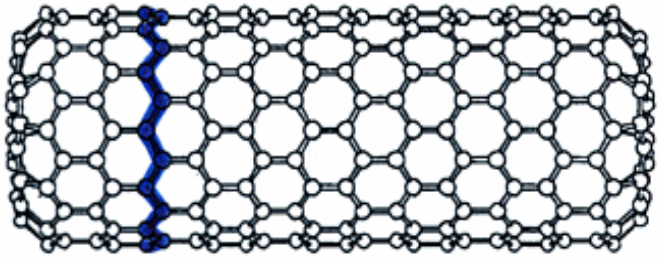
Single-Wall Carbon Nanotubes?:



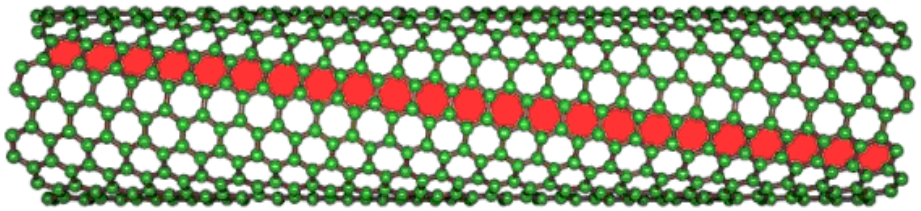
(n,n)
armchair



(n,0)
zigzag

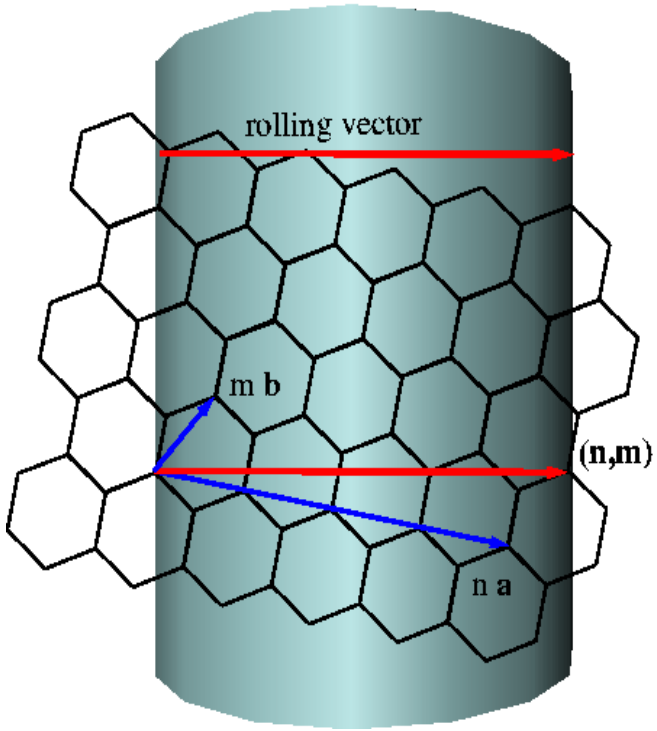


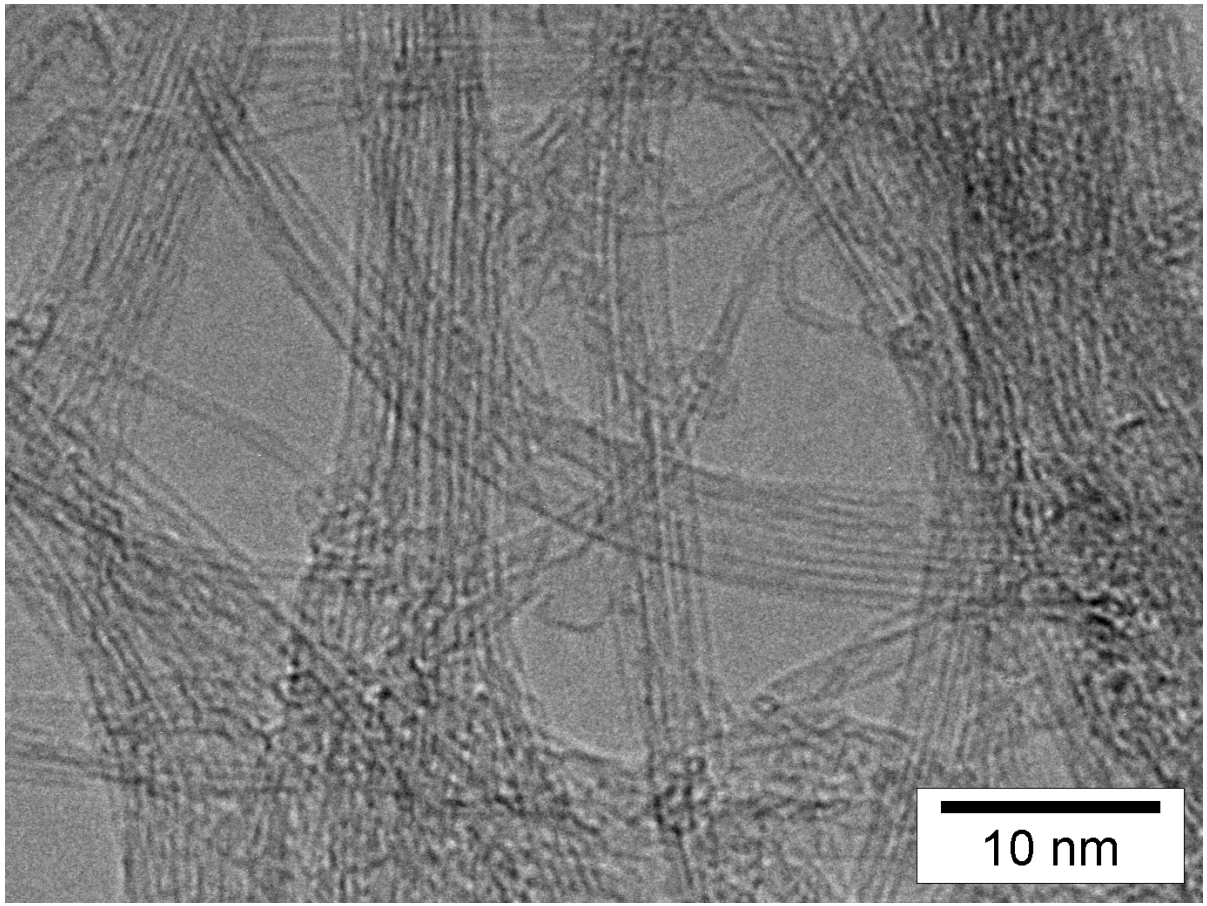
(n,m)
chiral



Roll up vector determines physical properties, electronic nature and surface interactions.

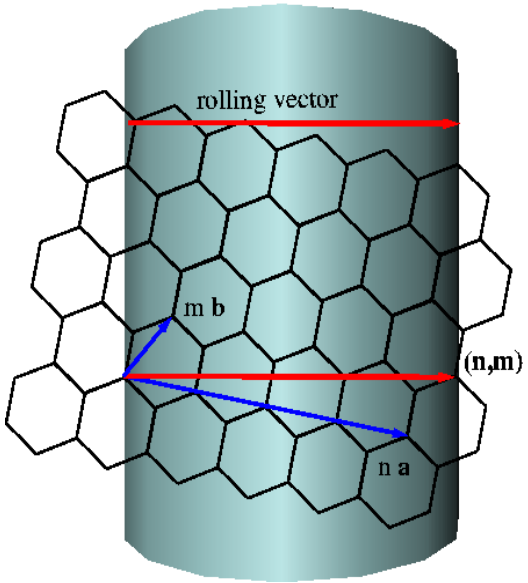
Single-Wall Carbon Nanotubes?:





Roll up vector determines physical properties, electronic nature and surface interactions.

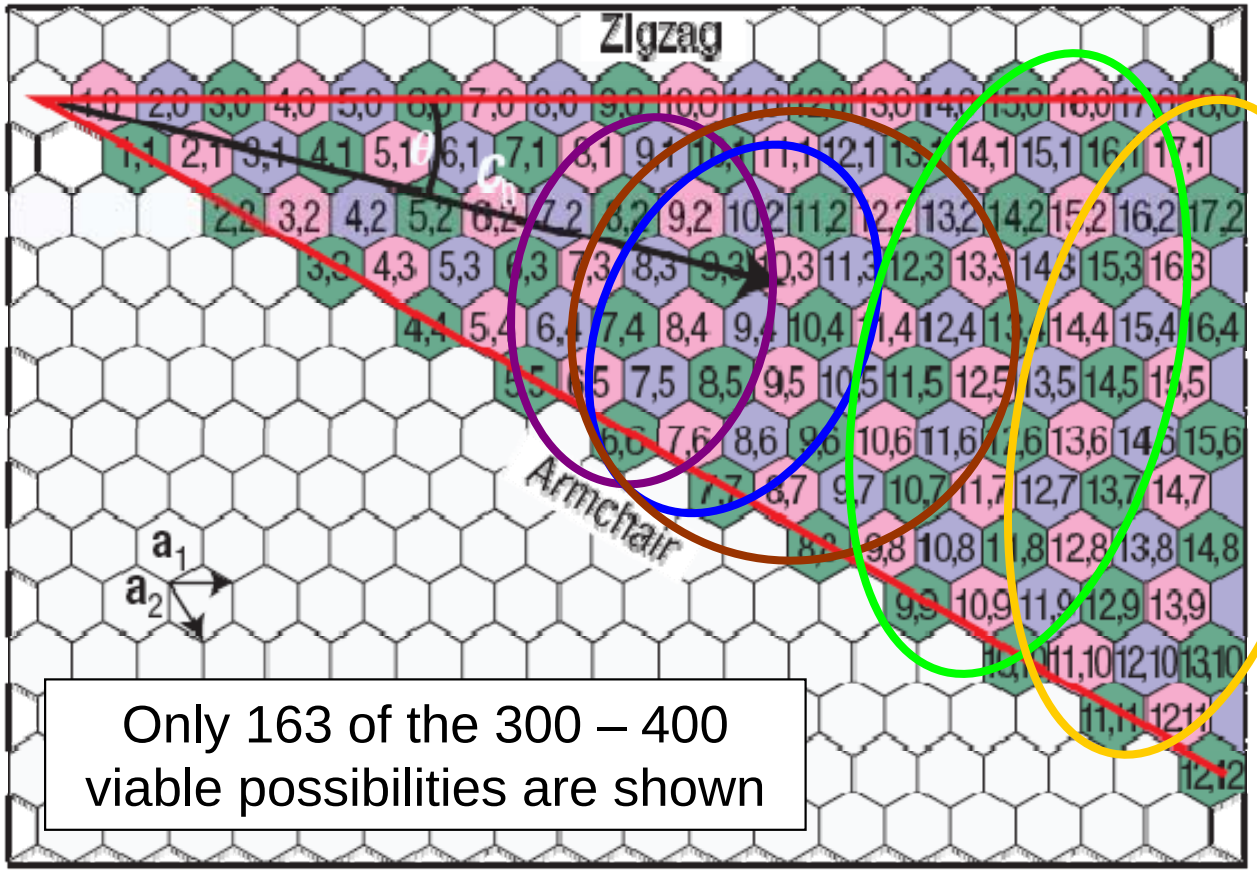
Polydispersity Problem



Hundreds of stable nanotubes

Synthetic methods generate multiple tubes with different properties

All tube types potentially useful



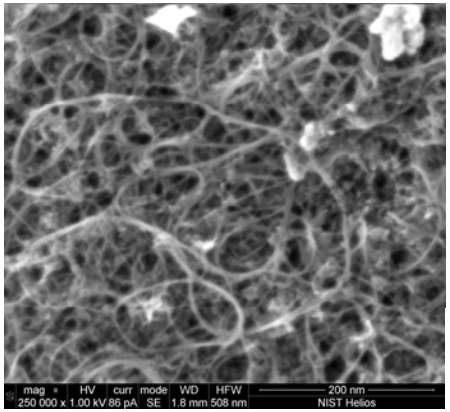
From Hersam, M. *Nature Nanotechnology* **2008**

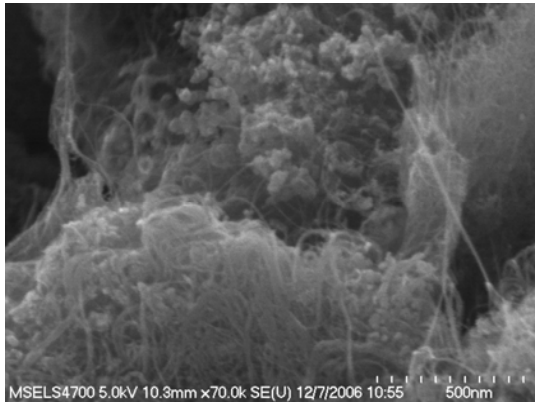
Green: Metallic, Pink, Purple: Semi-conducting

Polydispersity Problem

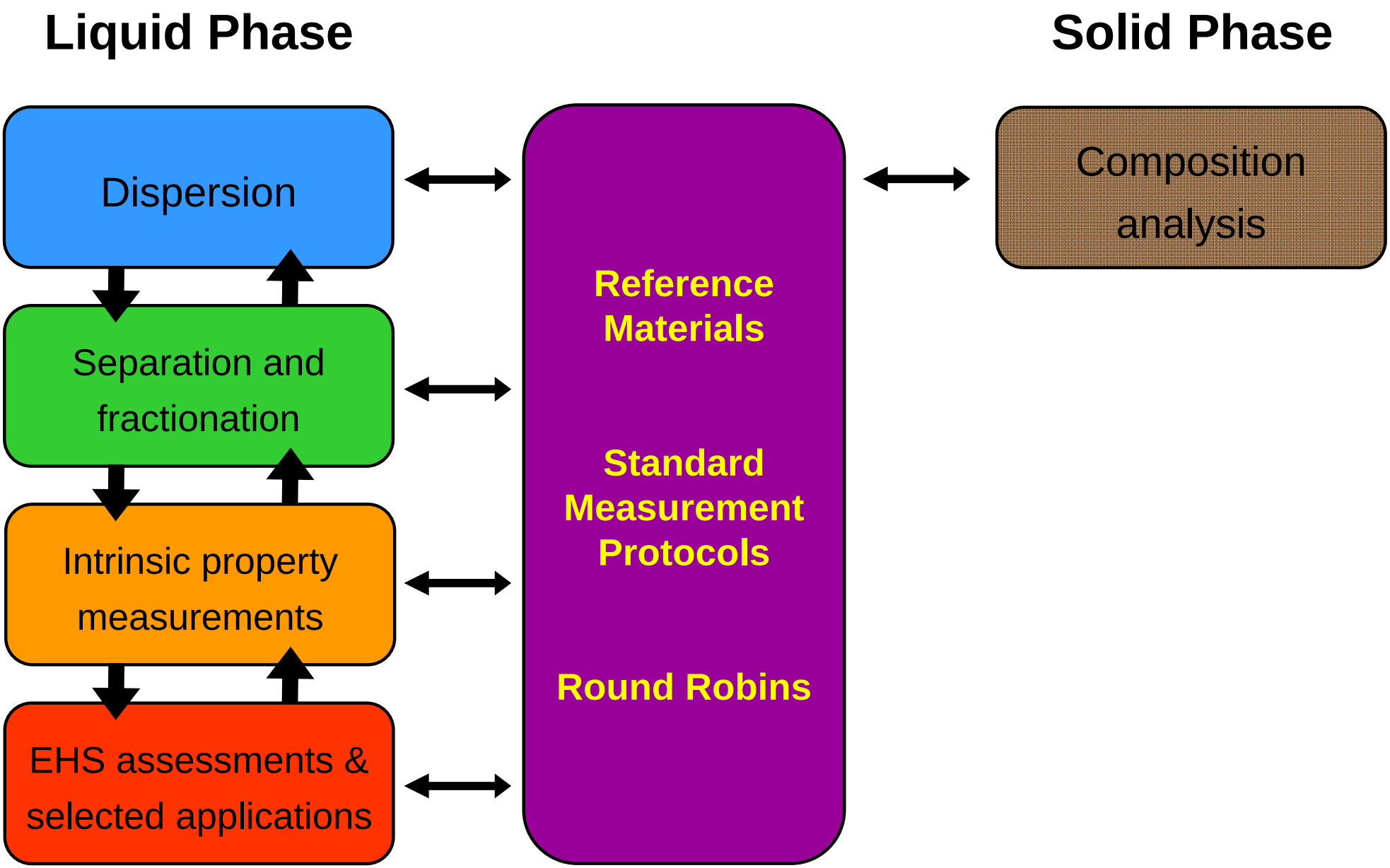
ALL SAMPLES are DIFFERENT

SWCNT length distribution, powder morphology, impurity content all vary batch to batch (or even within a batch) and across manufacturers.

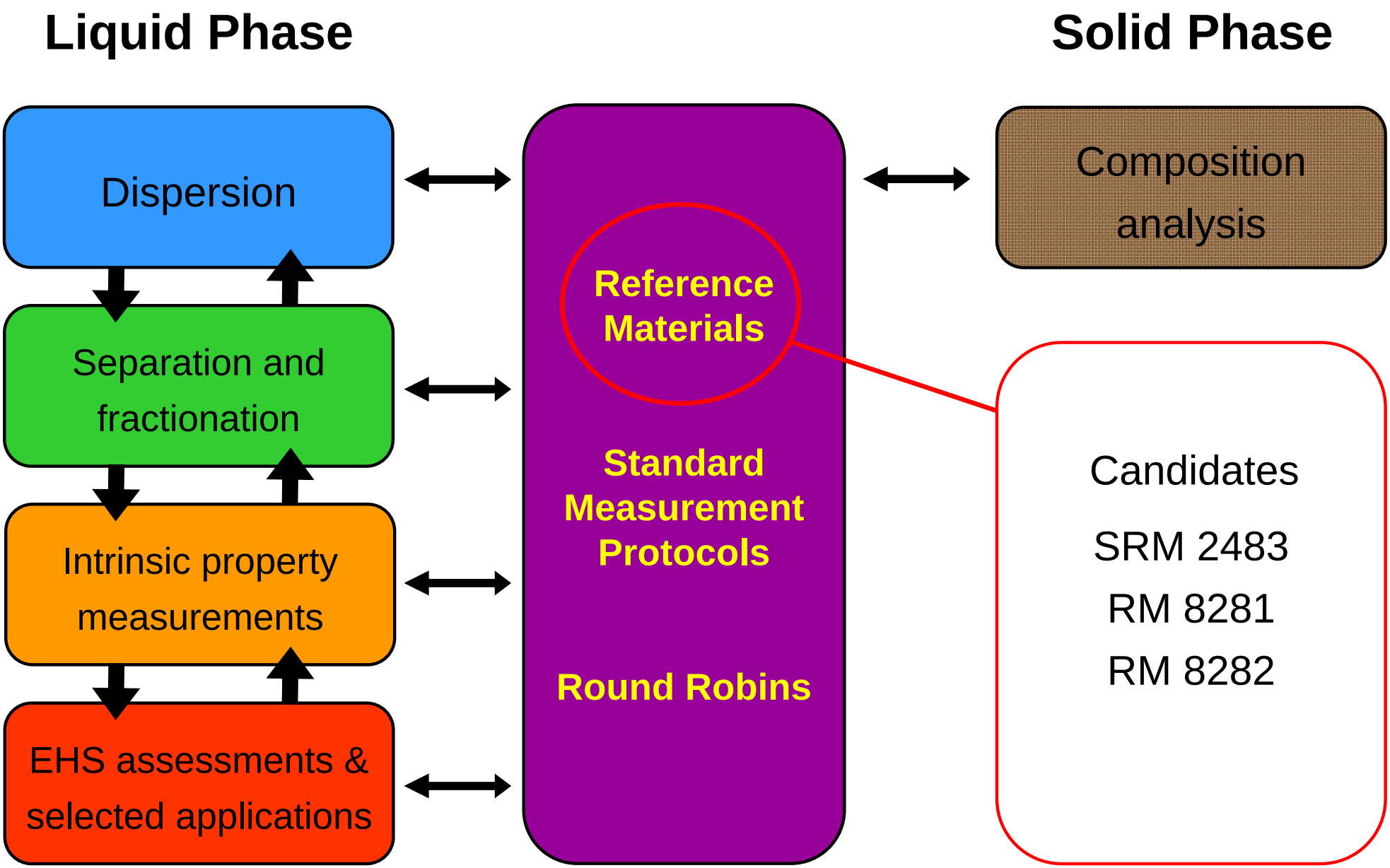




Nanotube Metrology Program



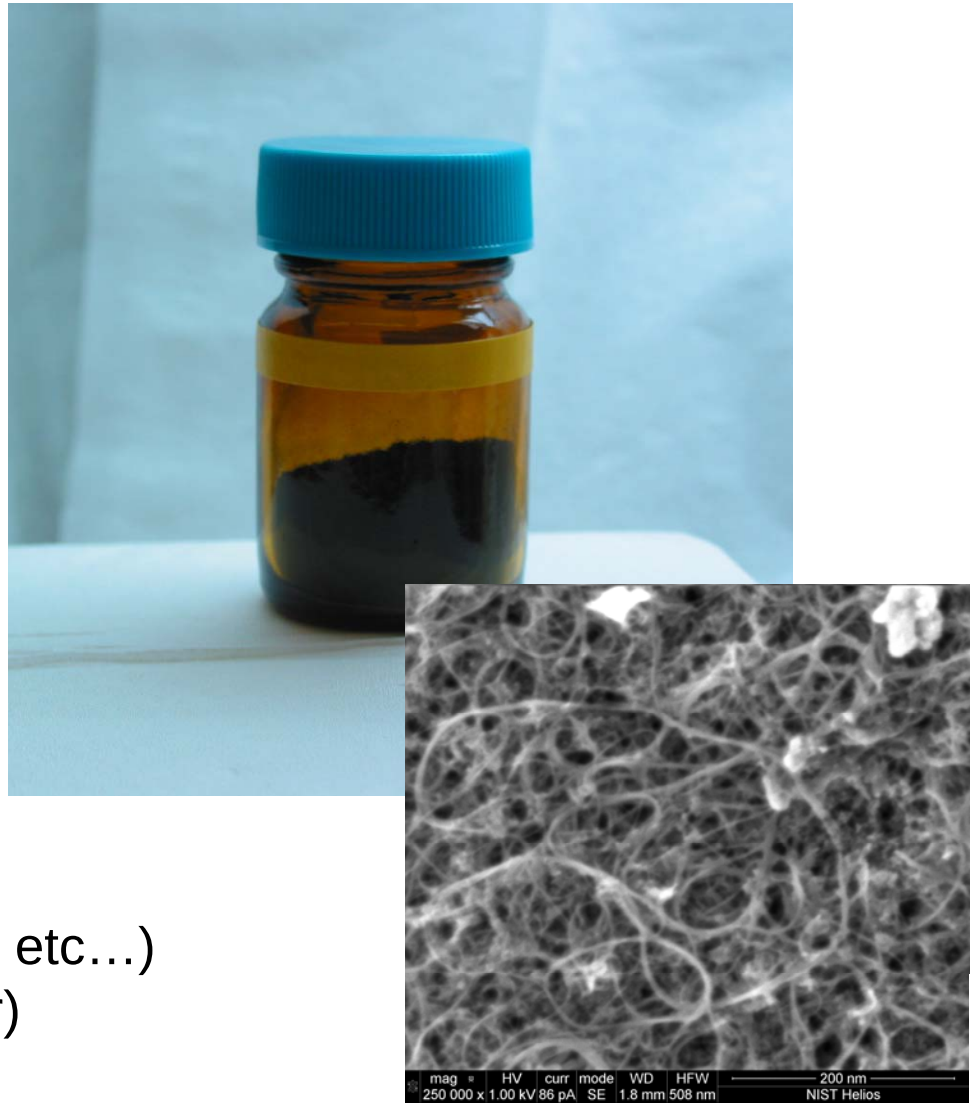
Nanotube Metrology Program



Raw Soot (Candidate SRM 2483)

Elemental composition

- PGAA
- INAA
- TGA
- ICP-MS / OES
- μXRF

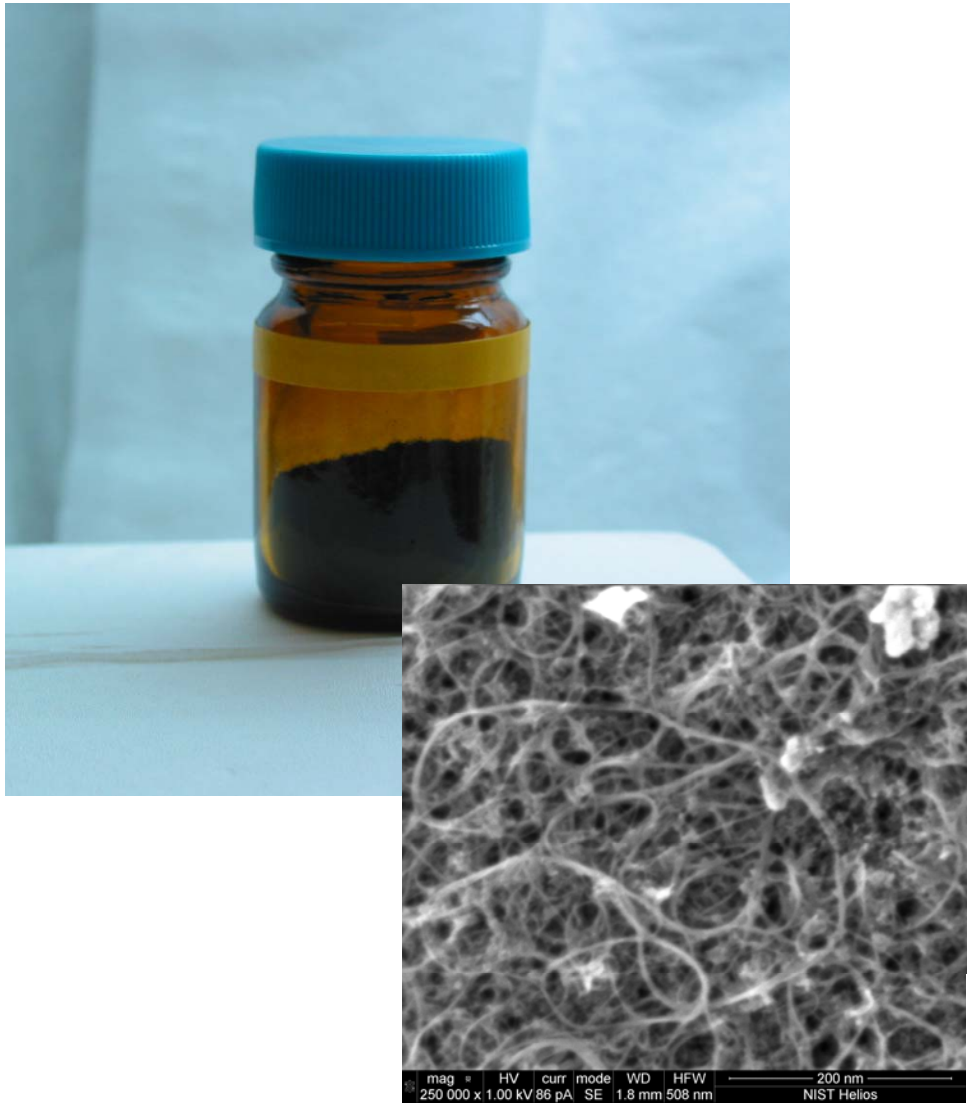


Techniques in collaboration with
Analytical Chem. (R. Zeisler, R. Spatz, L. Yu etc…)
Materials Reliability (E. Mansfield, S. Hooker)
Stat. Eng. Div. (S. Leigh)

Photograph and SEM micrograph of SWCNT soot.

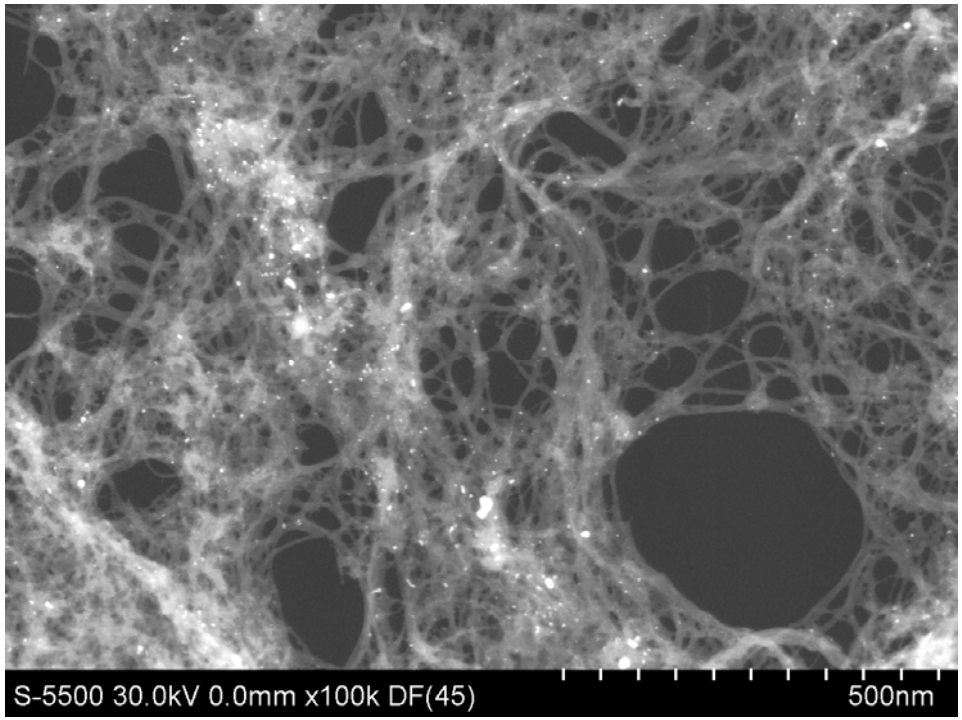
Raw Soot (Candidate SRM 2483)

- ≈ 0.26 g lots
- Certified for elemental composition.
- Informational Values
  - Diameter distribution
  - Raman spectra
  - Processing Data

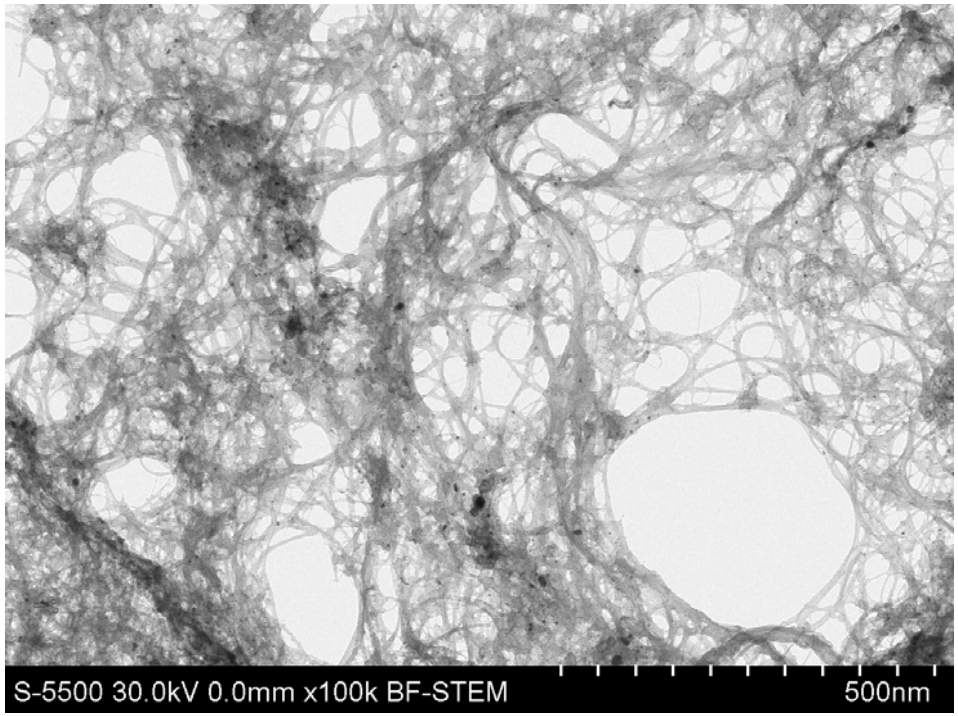


Photograph and SEM micrograph of SWCNT soot.

SRM 2483



High-angle backscattered electron image of the same field as the previous figure. Note the bright metal catalytic particles. (Field of view = 1280 nm).



Transmitted electron image note that the high electron density particles (dark) coincide with the bright particles of the previous figure. (Field of view = 1280 nm)

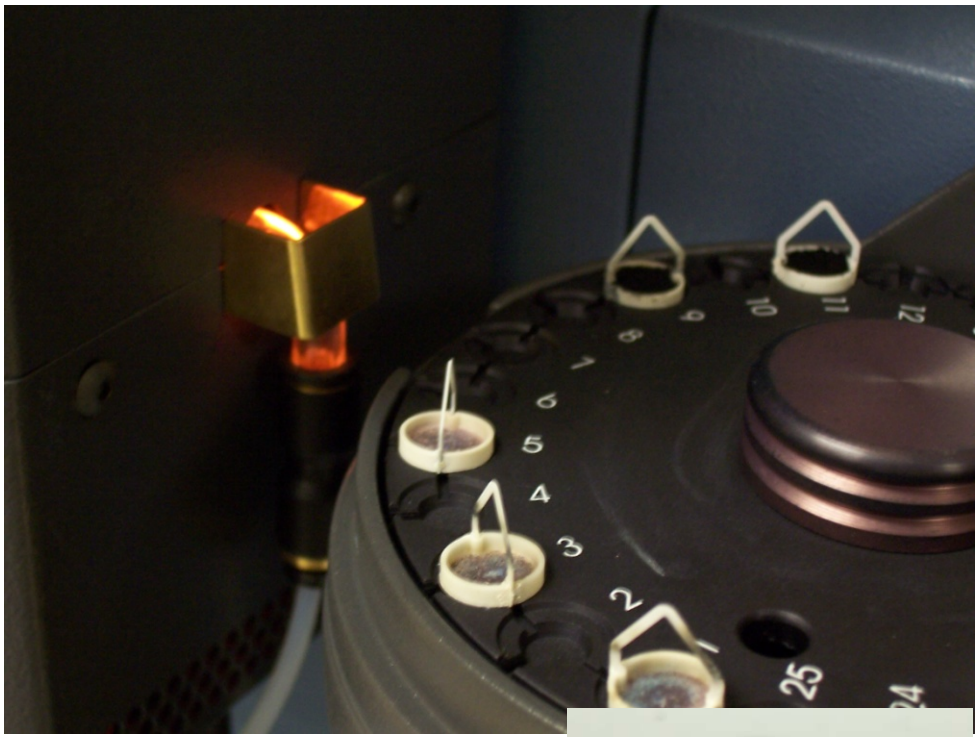
Courtesy of Michael Postek, NIST (MEL)

SRM 2483

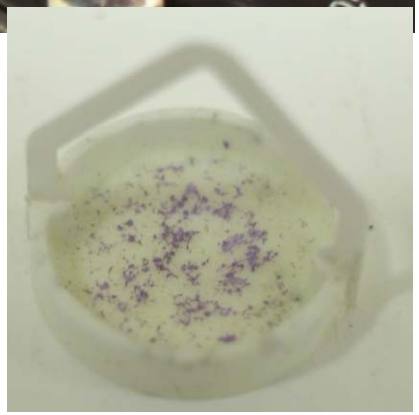
TGA Analysis of CNT Materials

Monitors the weight remaining as a function of temperature

~ 5 mg of material heated at 10 °C/min to 800 °C in flowing air and ceramic pans

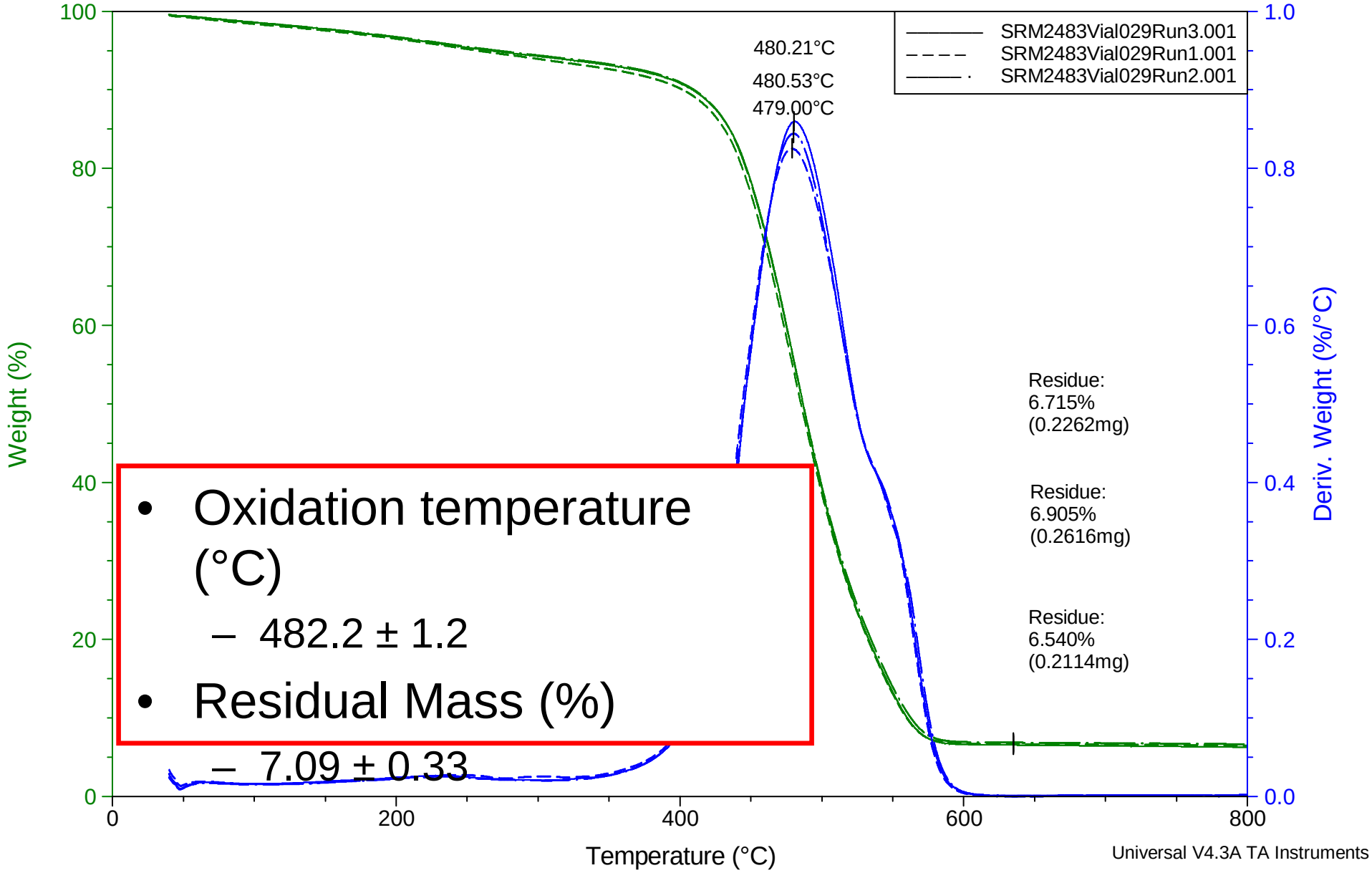


- 3 samples per RM vial
  - Vials stored in dessicator before and after sampling



Metallic residue

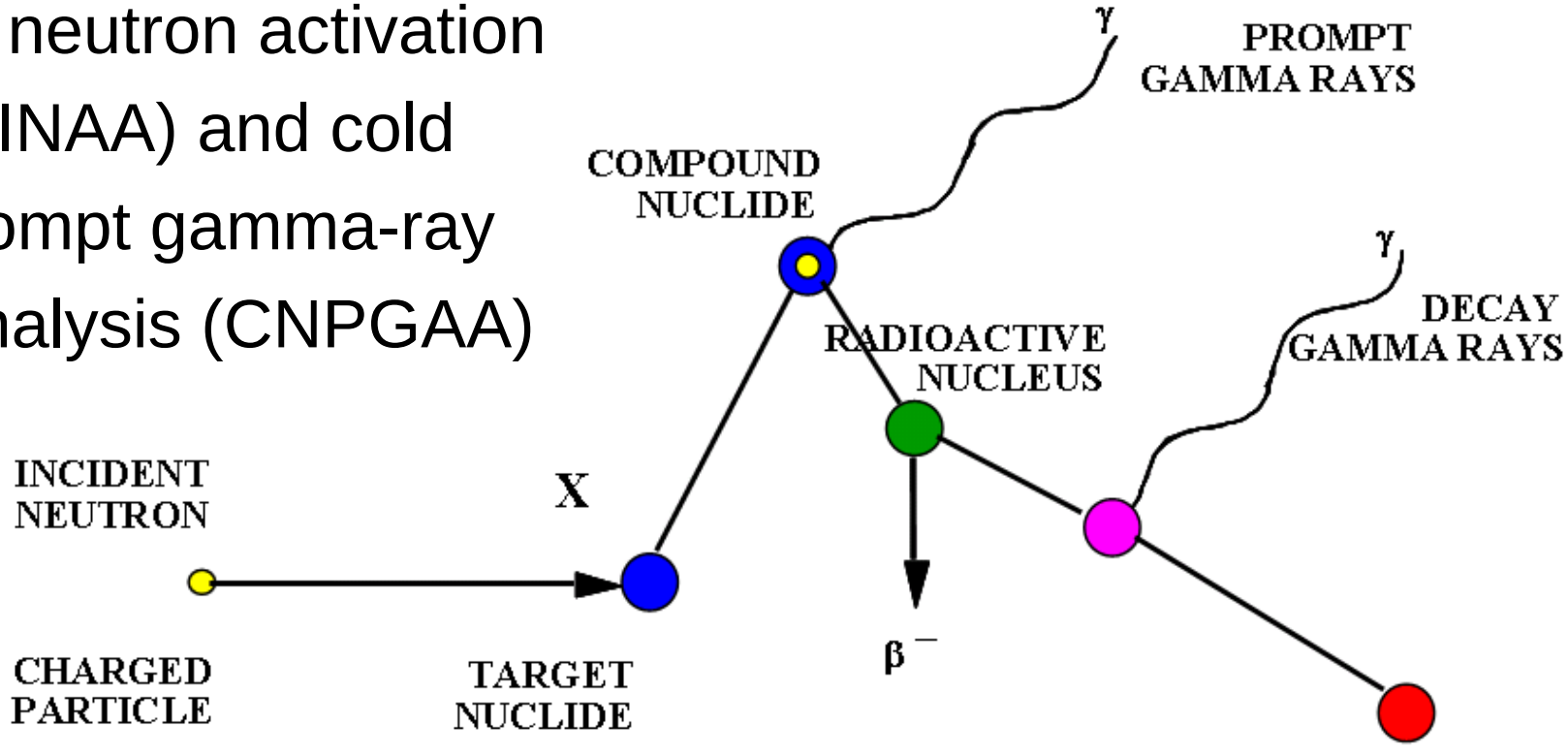
Reference Material Consistency



- Oxidation temperature (°C)
  - 482.2 ± 1.2
- Residual Mass (%)
  - 7.09 ± 0.33

SRM 2483

Residual catalyst concentrations measured by instrumental neutron activation analysis (INAA) and cold neutron prompt gamma-ray activation analysis (CNPGAA)



$$\frac{N_{x,unk}}{N_{x,std}} = \frac{A_{0,unk}(<\sigma>\phi\Gamma\varepsilon)_{std}}{A_{0,std}(<\sigma>\phi\Gamma\varepsilon)_{unk}}$$

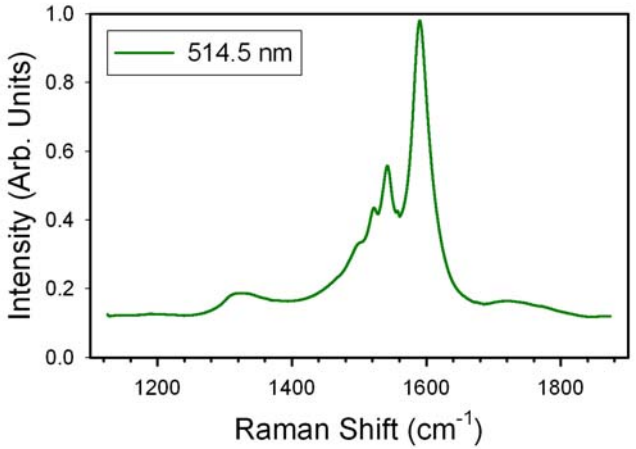
SRM 2483

Activation analysis results (INAA & PGAA)

Measurand	Mass Fraction Unit	Mass Fraction Value	Expanded Uncertainty (k=2)	Statistical Method	Analysis Methods
Certified Values					
Ba	mg/kg	119.0	3.4	DSL-HHD	A, B
Ce	mg/kg	192.7	7.3	DSL-HHD	A, B
Cl	%	0.2125	0.0089	DSL-HHD	A, C
Co	%	0.963	0.017	DSL-HHD	A, C
Dy	mg/kg	8.36	0.17	DSL-HHD	A, B
Eu	mg/kg	2.27	0.13	DSL-HHD	A, B
Gd	mg/kg	10.57	0.95	DSL-HHD	B, C
La	mg/kg	104.0	4.0	DSL-HHD	A, B
Mo	%	3.406	0.029	DSL-HHD	A, C
Sm	mg/kg	13.09	0.90	DSL-HHD	A, B, C
Reference Values					
Al	mg/kg	723	19	MLE	A
Mg	%	0.1150	0.0011	MLE	A
Mn	mg/kg	4.482	0.041	MLE	A
Na	%	0.1196	0.0014	DSL-HHD	A
Th	mg/kg	25.7	4.4	DSL-HHD	A, B
V	mg/kg	6.89	0.14	MLE	A
W	mg/kg	7.50	1.22	DSL-HHD	A, B
Information Values					
As	mg/kg	12.5			A
B	mg/kg	74.7			C
C	%	94.6			C
Ca	%	0.303			A
Cu	mg/kg	186			A
H	%	0.38			C

Analytical Techniques Used

A	Instrumental neutron activation analysis (INAA)
B	Inductively coupled plasma mass spectrometry (ICP-MS)
C	Prompt gamma activation analysis (PGAA)

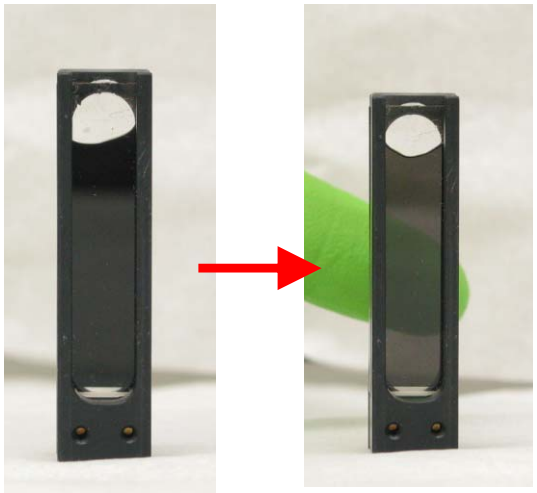


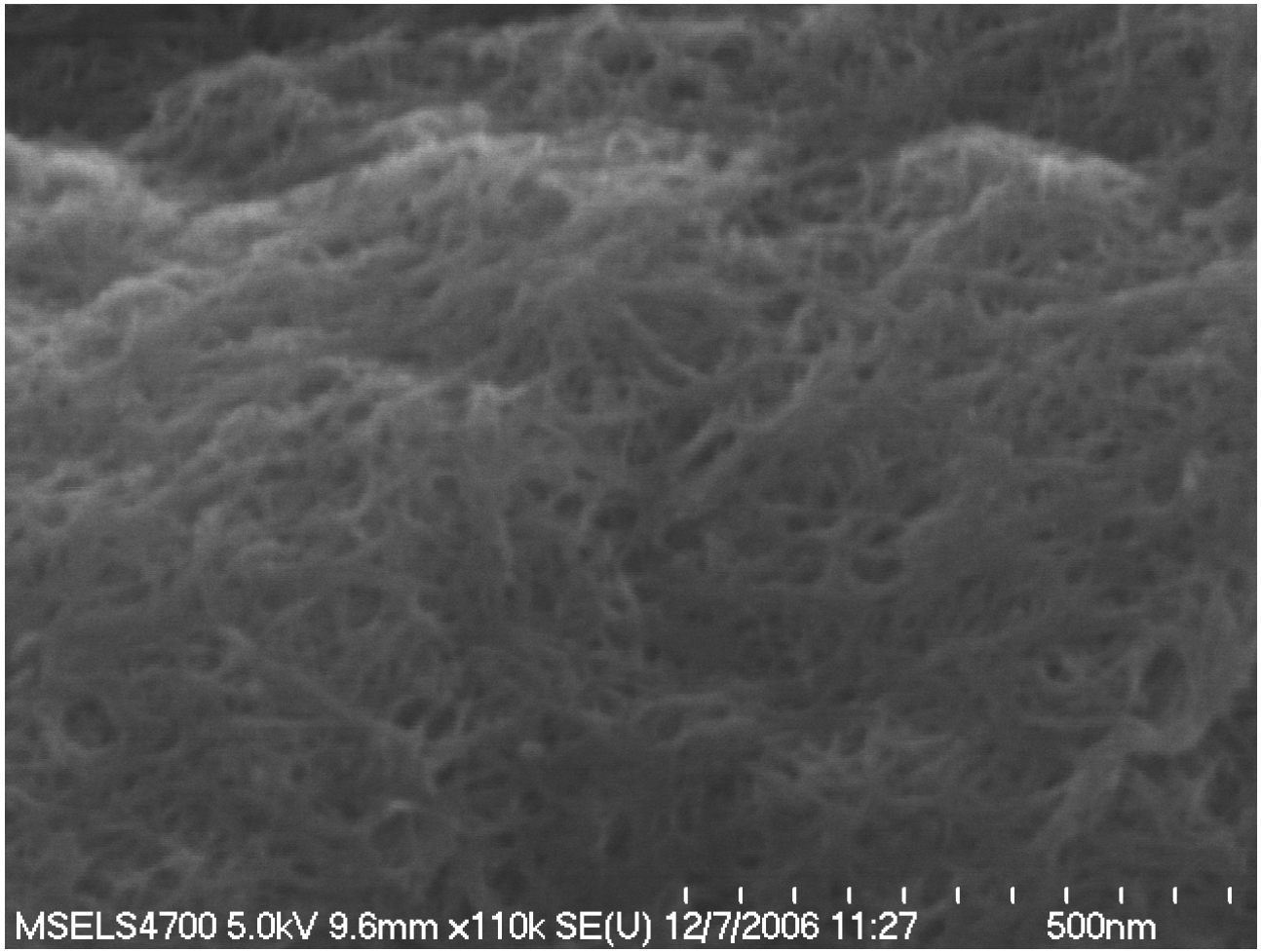
Additional informational values available for Raman scattering, absorbance, chiral distribution

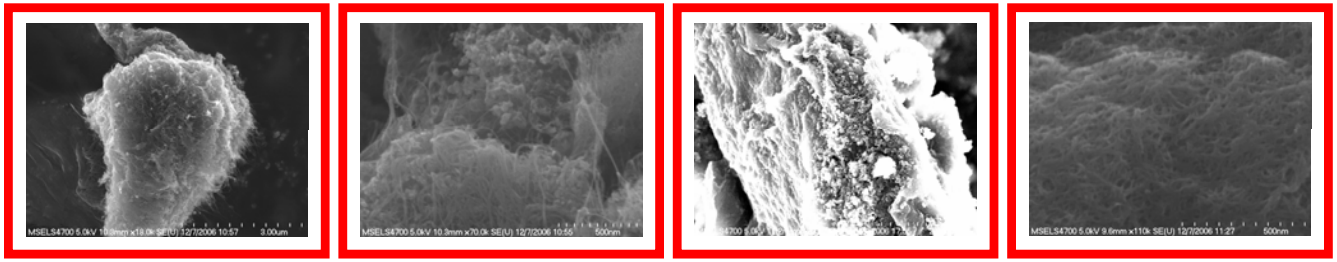
Water Content

5.18 ± 0.32 % no drying

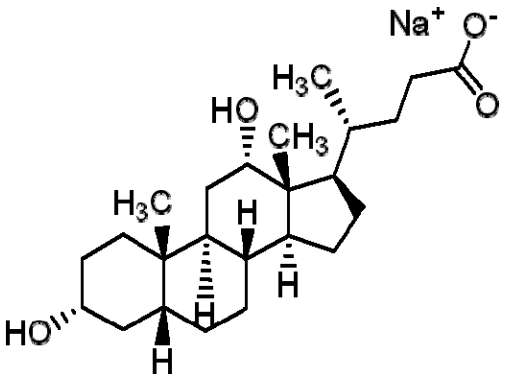
Dispersion



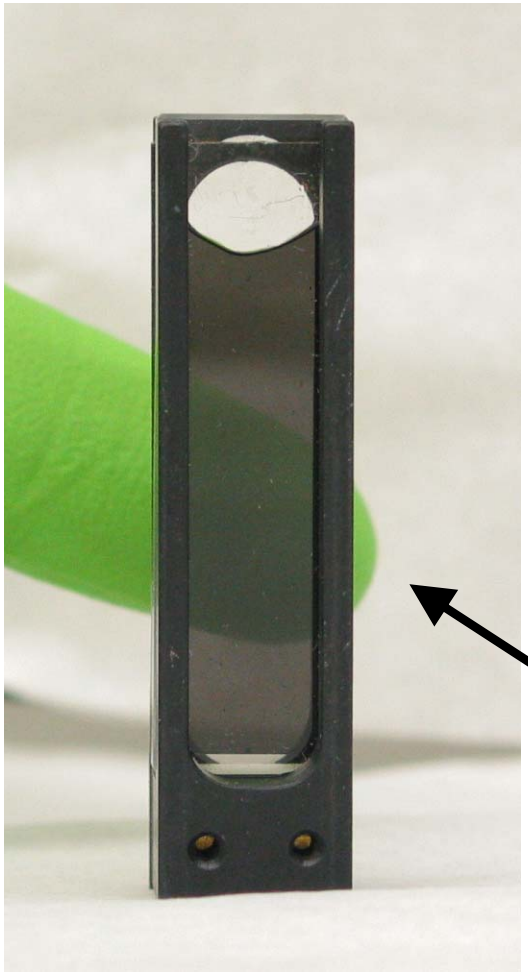




Dispersion



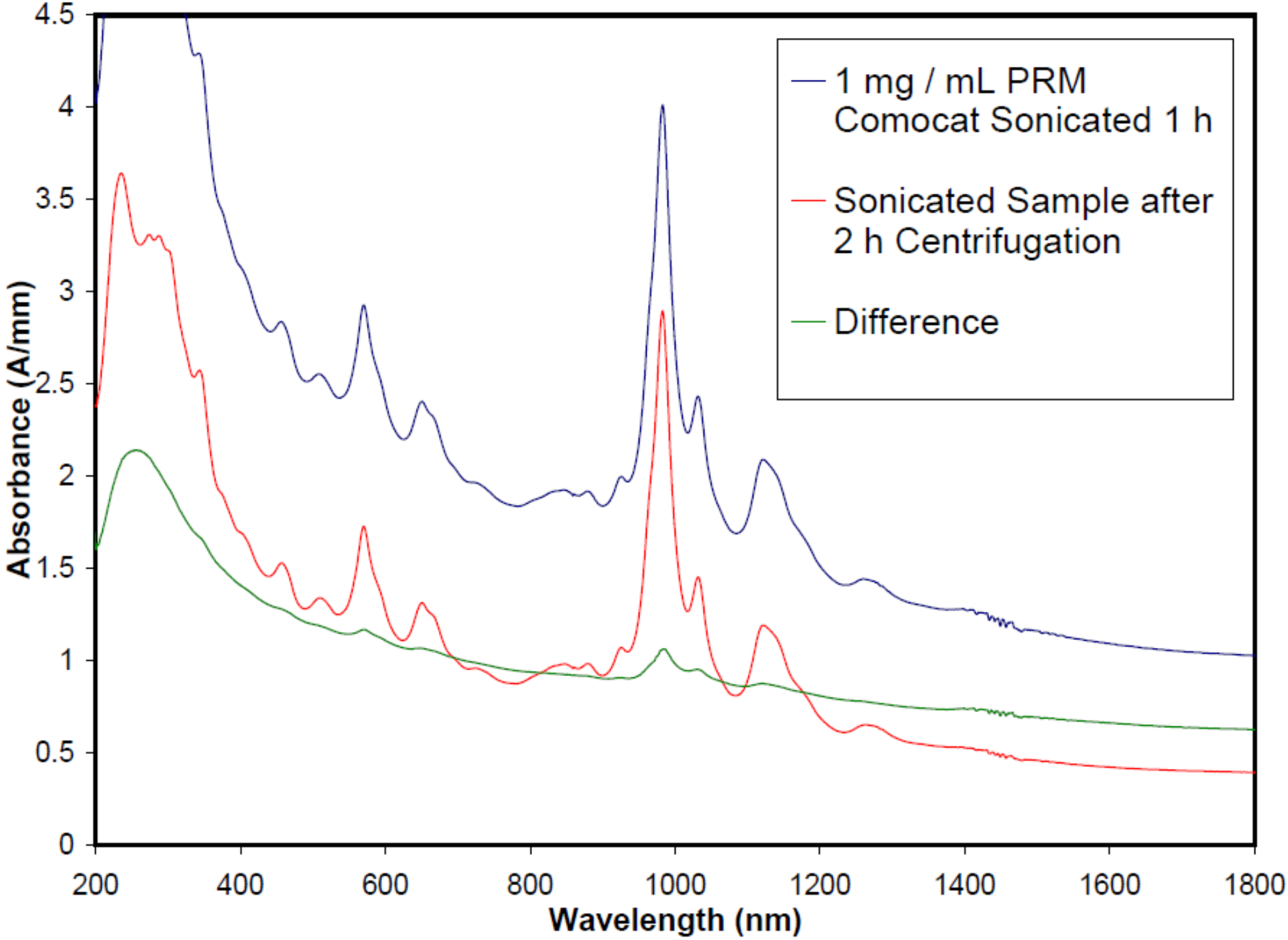
Deoxycholate



1 hour Sonication
at ≈ 1 W / mL
in 2 % mass/vol surfactant

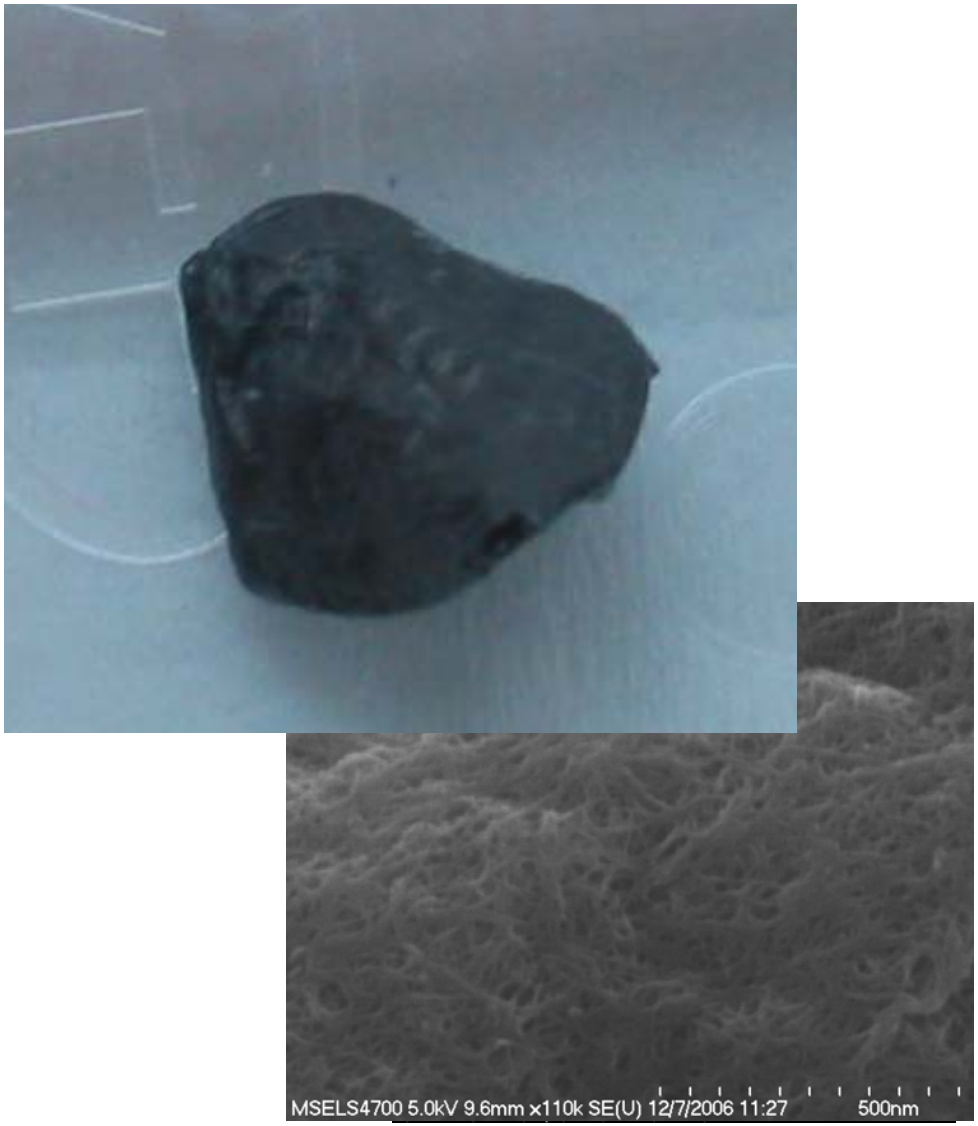
2 h Centrifugation
at ≈ 40 000 g

Supernatant


1 mg / mL PRM
Comocat Sonicated 1 h
Sonicated Sample after
2 h Centrifugation
Difference
Absorbance (A/mm)
Wavelength (nm)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
200
400
600
800
1000
1200
1400
1600
1800

Purified Buckypaper RM

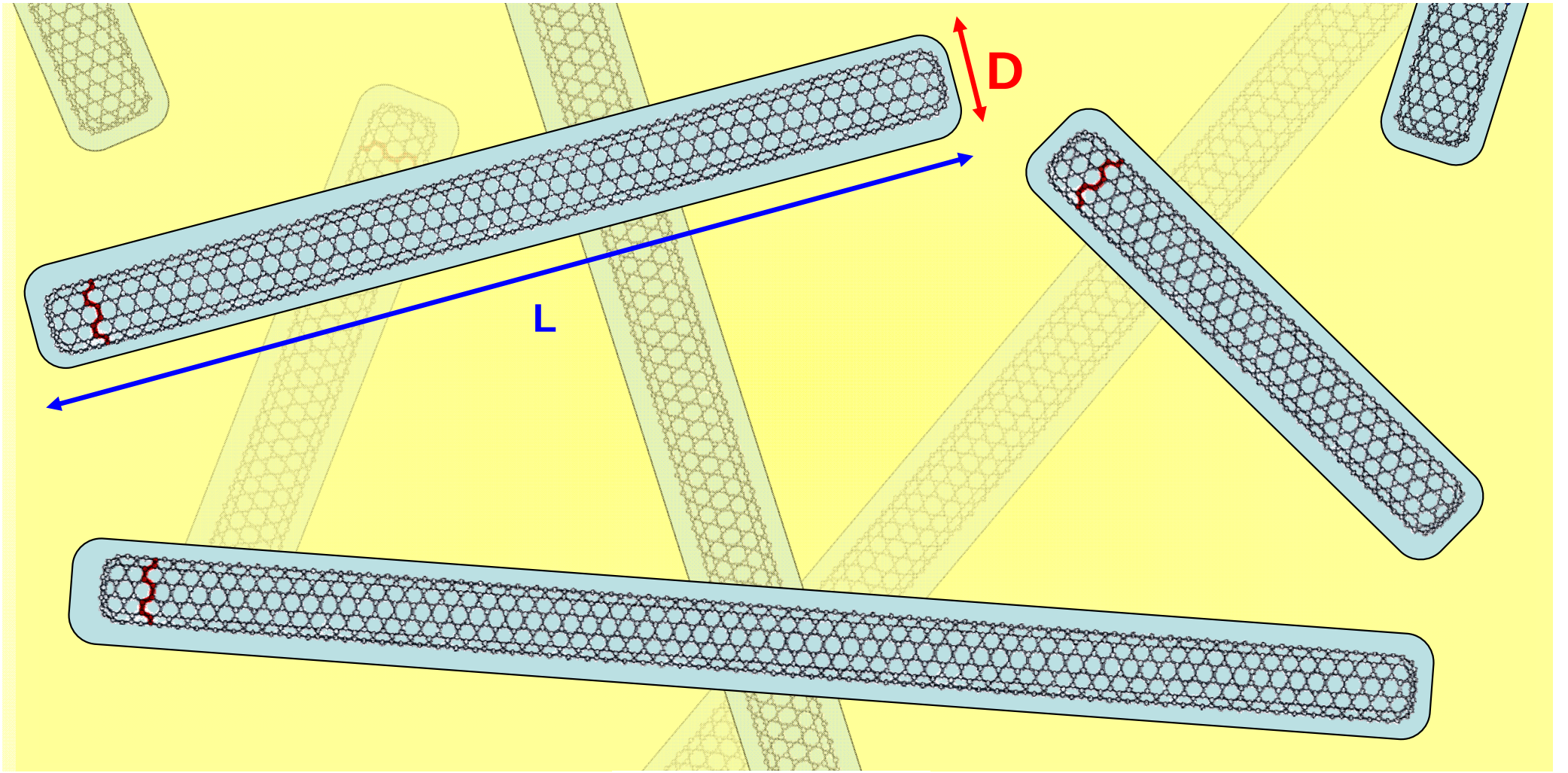
- Purified Soot (RM 8282).
- Information on elemental composition.
  - TGA
  - Neutron Methods
- Informational Values
  - Diameter distribution
  - Raman spectra
  - Microscopy



Representative Photograph and SEM micrograph of SWCNT paper.

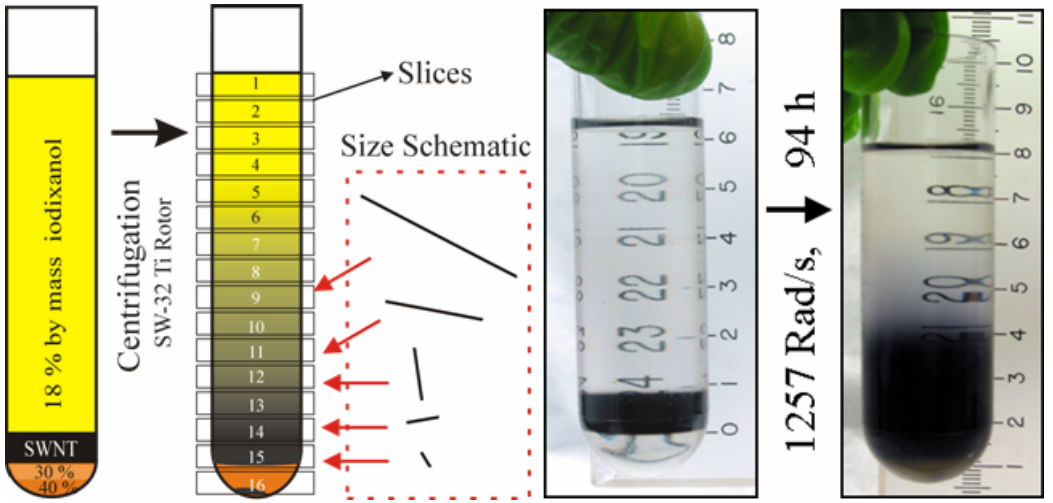
Carbon Nanotubes:

After dispersion, the individualized SWCNTs have a nearly uniform diameter, but a vast length distribution.



Centrifugation Based Length Separation

We can take advantage of the length dependence of the friction coefficient for a rod to enable length separation!



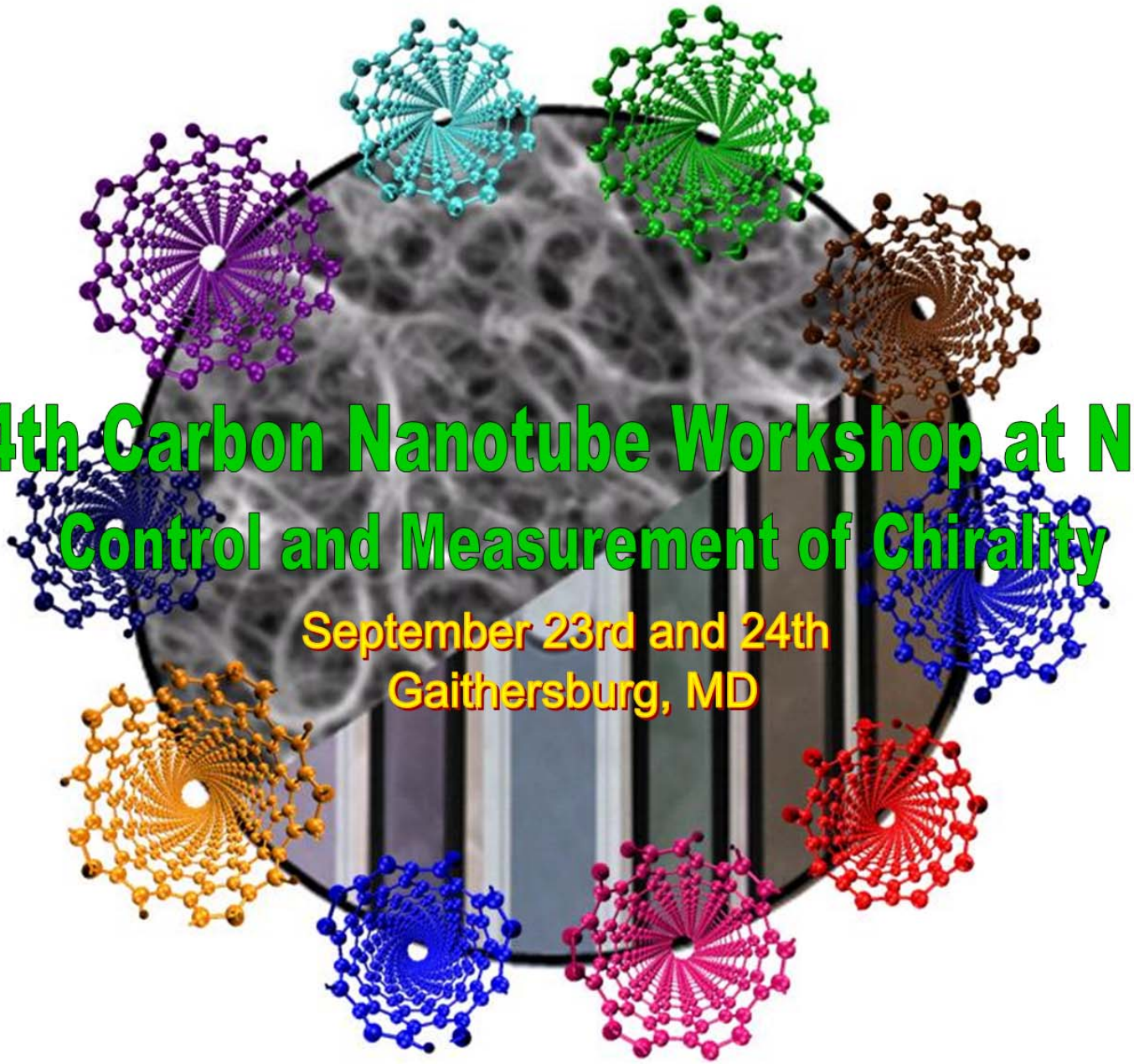
$$N_i(\ell) \approx c_i \frac{(\rho_s - \rho_{SWCNT,i}) G r^2}{6\eta} \frac{2\gamma^4 + 0.614\gamma^3 + 0.544\gamma^2 - 0.136}{\gamma^3 + 0.614\gamma^2 + 0.638\gamma + 0.0135}$$

With correct set up the nanotube flux will be length dependent, with longer tubes moving faster.

Length Populations RM 8281

- Specified average lengths
  - ~ 0.8 μm
  - ~ 0.4 μm
  - ~ 0.15 μm
- Informational Values
  - Diameter distribution
  - Raman spectra
  - Processing Data

Photograph of length separated carbon nanotubes dispersed in surfactant solution.

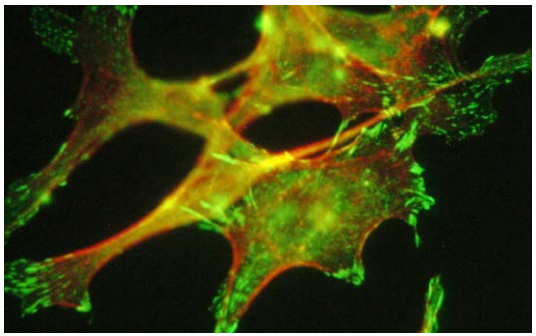


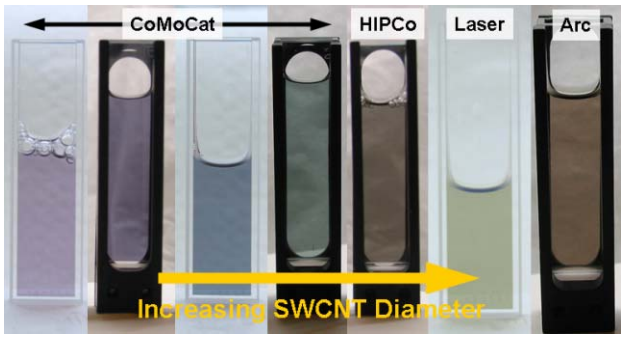
The 4th Carbon Nanotube Workshop at NIST:
Control and Measurement of Chirality

September 23rd and 24th
Gaithersburg, MD

Summary:

- To address the metrology needs for nanotubes we are working on releasing SWCNT reference materials.
  - SRM 2483: Raw Nanotube Soot
  - RM 8282: Purified Nanotube Bucky Paper
- RM 8281 Length sorted nanotubes in aqueous dispersion
- A workshop on chirality measurement, separation, and applications will be held at NIST in September.





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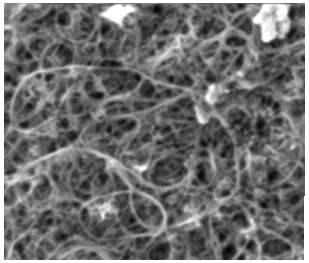
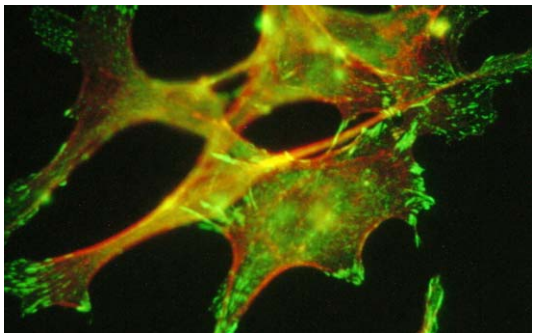
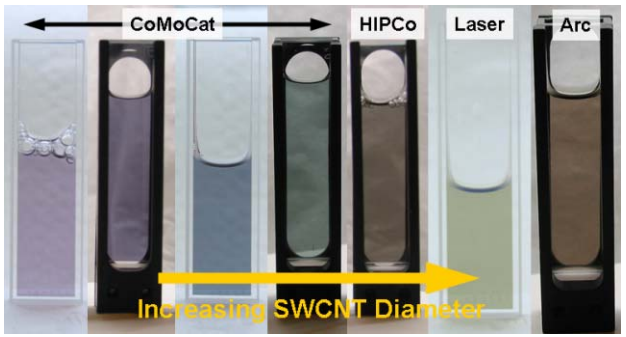
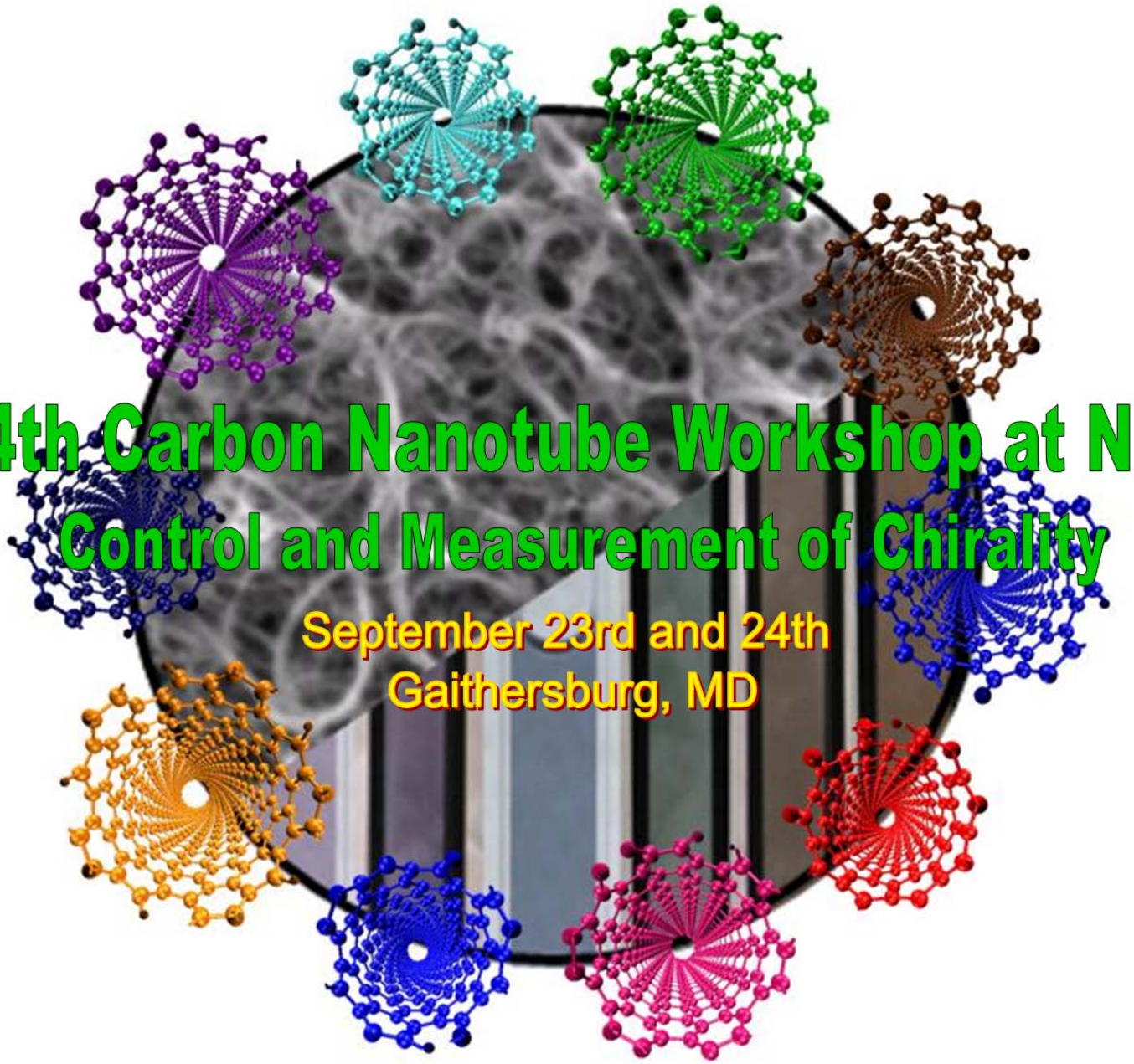


Questions?

Contact: jeffrey.fagan@nist.gov







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

September 23rd and 24th
Gaithersburg, MD