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From **Discovery** to **Innovation...**

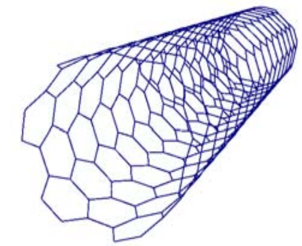
Challenges in the Characterization of Carbon Nanotubes: the Need for Standards

Chris Kingston

Molecular and Nanomaterial Architectures Group

Tri-National Workshop on Standards for Nanotechnology
February 7, 2007

Single Walled Carbon NanoTubes
(*SWNT*)



Perfection! at the molecular level

"The strongest, stiffest, toughest material, and the best thermal and electrical conductor known."

- Composites
- Electronics
- Energy
- Environment
- Health

Why has this potential not yet been realized?

What’s the holdup?

× ***Too much variability!***

Production

There are *many* production methods for SWNT, each producing material that is slightly different:

– diameter distribution, length distribution, chirality, purity, catalysts, impurity species, defects

Purification

Increases the fraction of nanotubes in the sample, but often modifies the SWNT themselves:

– open ends, reduced length, functional groups, defects

★*Applications will require certification of properties and function*

Characterization

- Nanotubes are nanometric carbon particles with a graphitic structure…
  - But so are many of the impurities!

- How do we distinguish between these materials to determine the quantity, quality, and properties of the nanotubes in the sample?

  Most Common Characterization Techniques:
    - Electron microscopy (SEM & TEM)
    - Raman spectroscopy
    - Thermal analysis (TGA/DTG)
    - Absorption spectroscopy (UV-Vis-NIR)

Outline

- Imaging
- Raman Spectroscopy
- Thermal Analysis
- Absorption Spectroscopy

Usefulness in characterizing SWNT samples

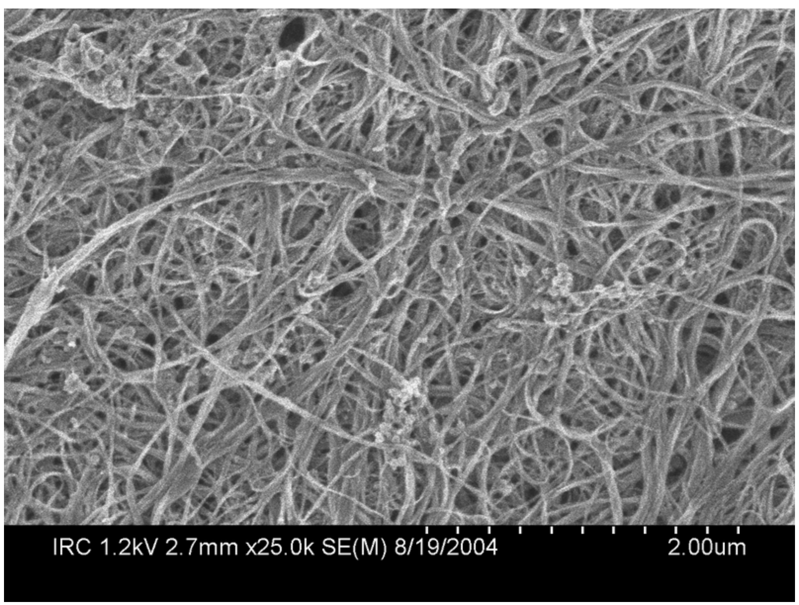
Limitations in the data produced and the conclusions that can be drawn

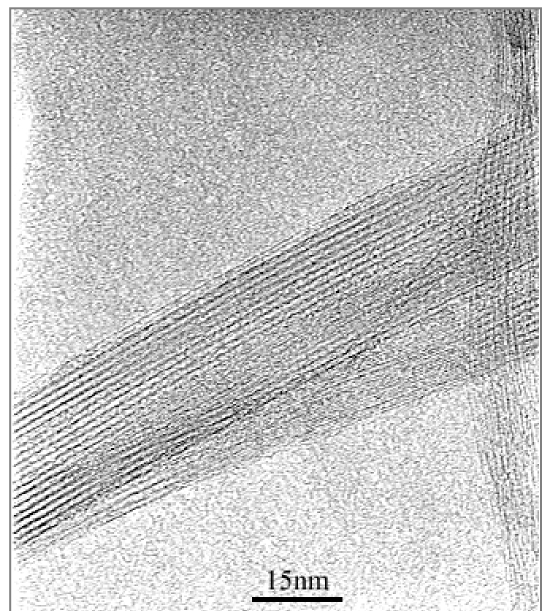
Imaging

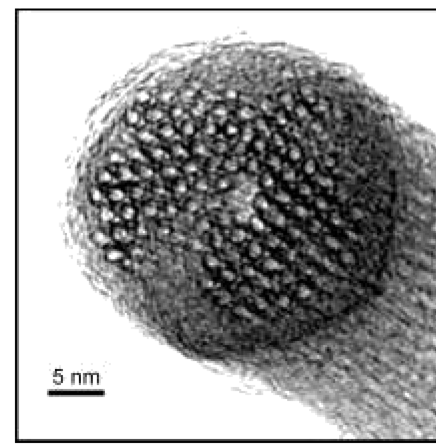
Electron microscopy is an essential tool for characterizing any nanomaterial

- direct observation of size, shape, structure

The only tools that let us *see* the material







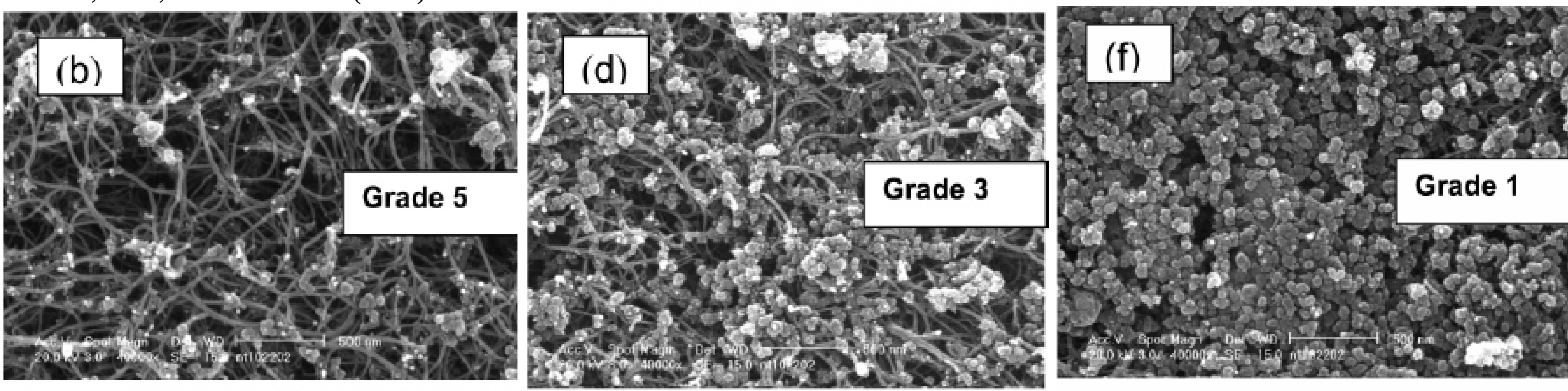
Kingston, et al., *Carbon* **42** 1657 (2004)

SEM

High Resolution TEM

How quantitative can imaging be?

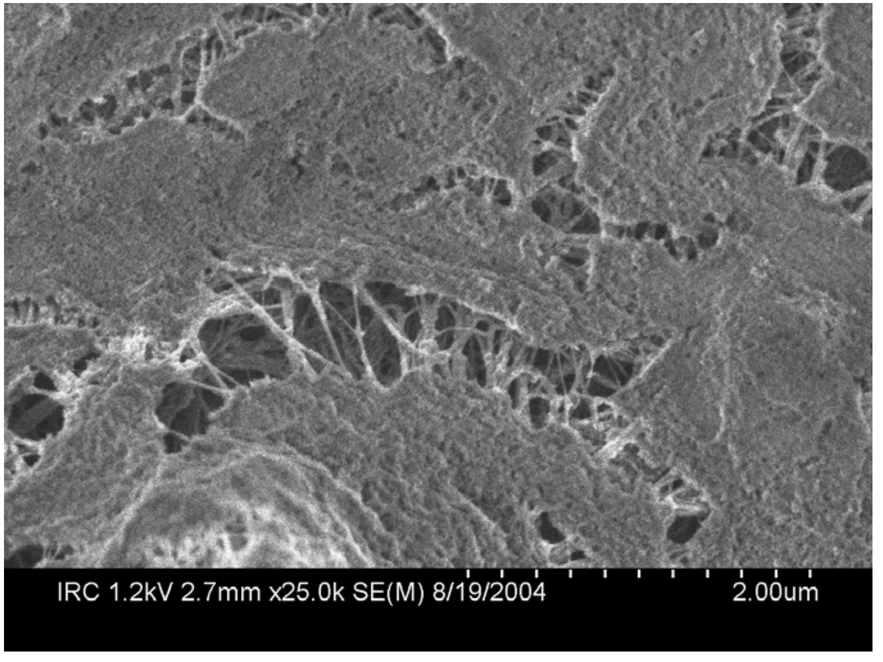
Itkis, et al., *JACS* **127** 3439 (2005)

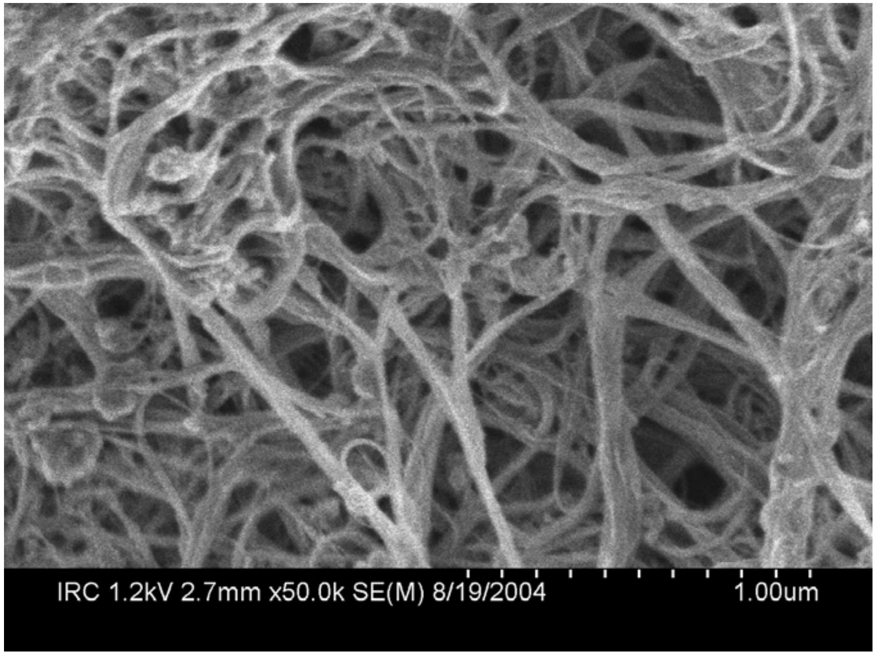


- These 3 images were taken from samples of the same production batch.

Material is not homogeneous throughout the entire batch.

How quantitative can imaging be?





- These 2 images were taken from the same SEM stub!

Material is not homogeneous across the entire sample.

Imaging Limitations

- Can only observe **~10^{-12} g** of sample in a typical SEM image; *much* less for TEM
  - There is no way to homogenize a sample down to that scale
- There are no current statistical tools for analyzing multiple images
  - How many would you need?
- Sample preparation can have a big impact

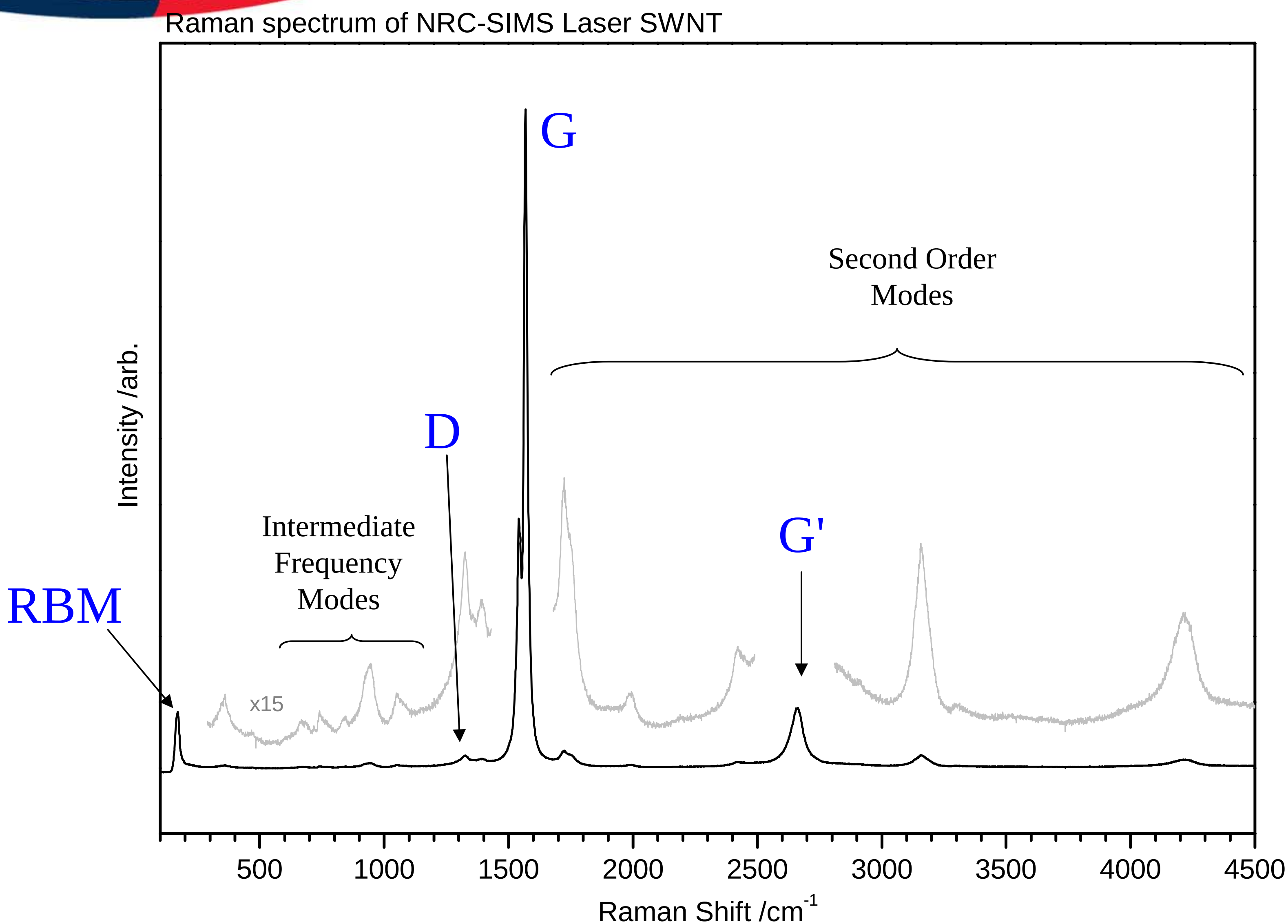
Quantitative

- diameter, length, bundle sizes, catalyst particle sizes

Qualitative

- surface coatings, impurity structures, relative concentrations

Raman Spectroscopy



Raman & SWNT

Raman Spectroscopy is an extremely powerful tool for characterizing SWNT

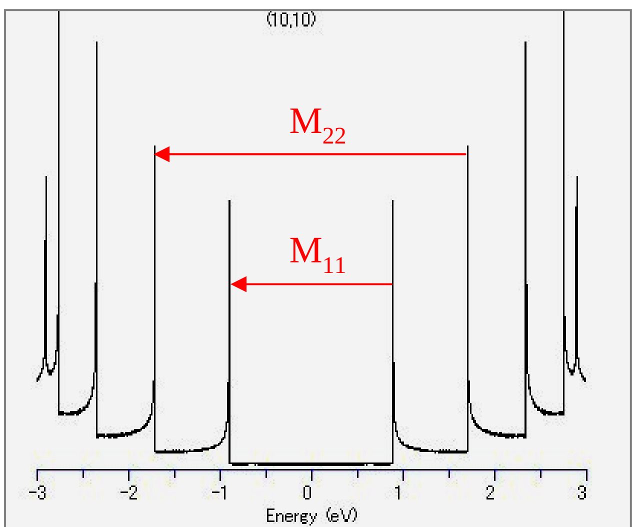
- Qualitative and quantitative information on:
  - Diameter
  - Electronic structure
  - Purity
  - Crystallinity
  - Distinguish Metallic and Semiconducting
  - Chirality (for single SWNT)

Must understand the fundamental process

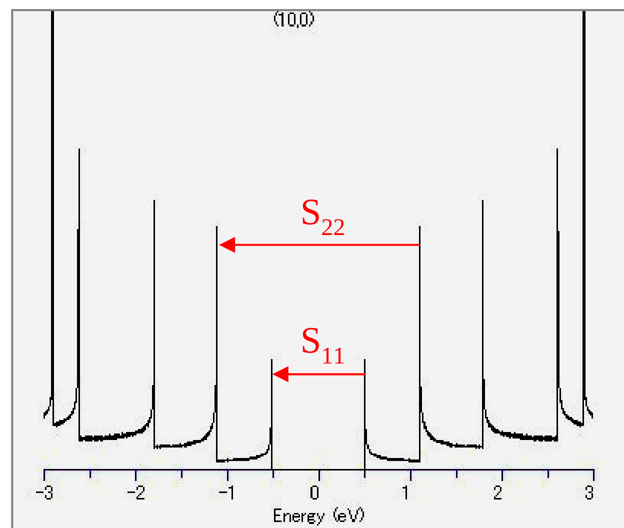
See: Dresselhaus, et al., *Adv Phys* **49** 705 (2000)

SWNT: Resonant Raman Process

- Only observe Raman scatter when the probing laser is in resonance with an electronic transition in the SWNT
- Typically only probing a sub-set of the SWNT in the sample

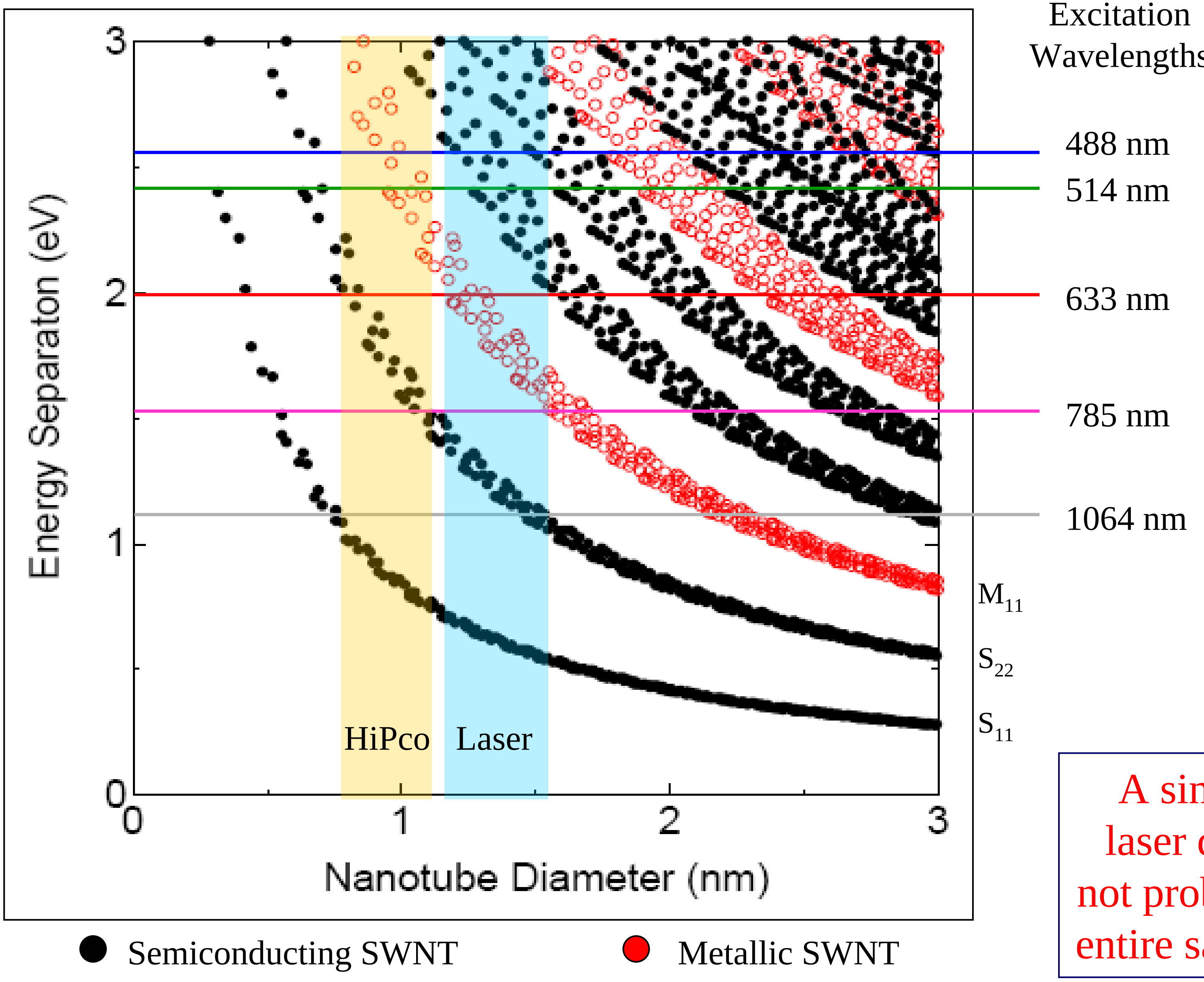


Metallic SWNT



Semiconducting SWNT

Resonant Excitation



A single laser does not probe the entire sample

Raman & Laser Power

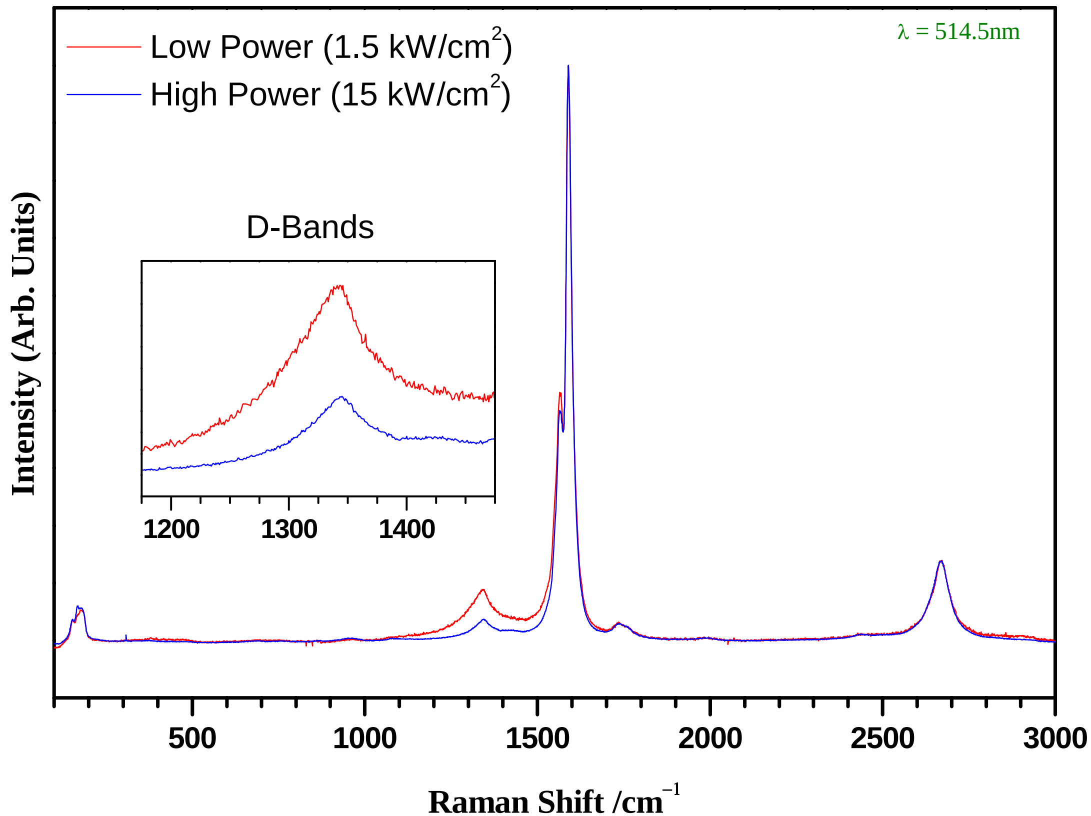
Raman signal increases with increasing laser power

BUT

Too much power can cause local heating in the sample

⬇

Oxidize some components of the sample, distorting the spectrum



See also: Zhang, et al., *Phys Rev B* **65** 073401 (2002)

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Raman Considerations

- compare against reference samples whenever possible
- sample preparation and morphology
- sample homogeneity
- laser energy versus diameter distribution
  - what are you in resonance with?
- laser power
  - too much power can burn your sample!
- one laser wavelength won’t probe all of the SWNT
- samples from different sources are difficult to compare

Thermal Analysis: TGA/DTG

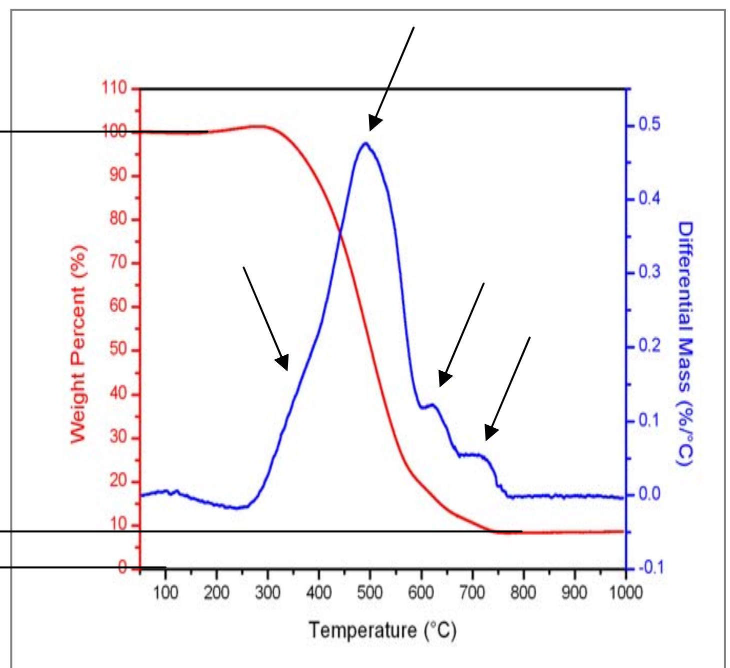
Controlled Oxidation process that gives quantitative data on the weight fractions of carbon and metal catalyst in the sample, and the temperatures of bulk oxidation events.

TGA

DTG

Carbon Content

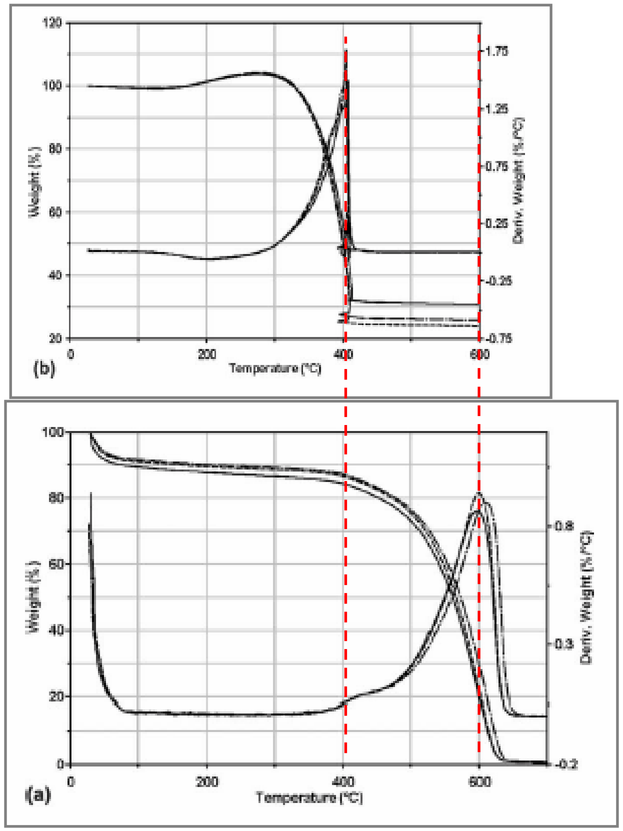
Metal Content



Discrete Oxidation Events

Interpretation

Raw

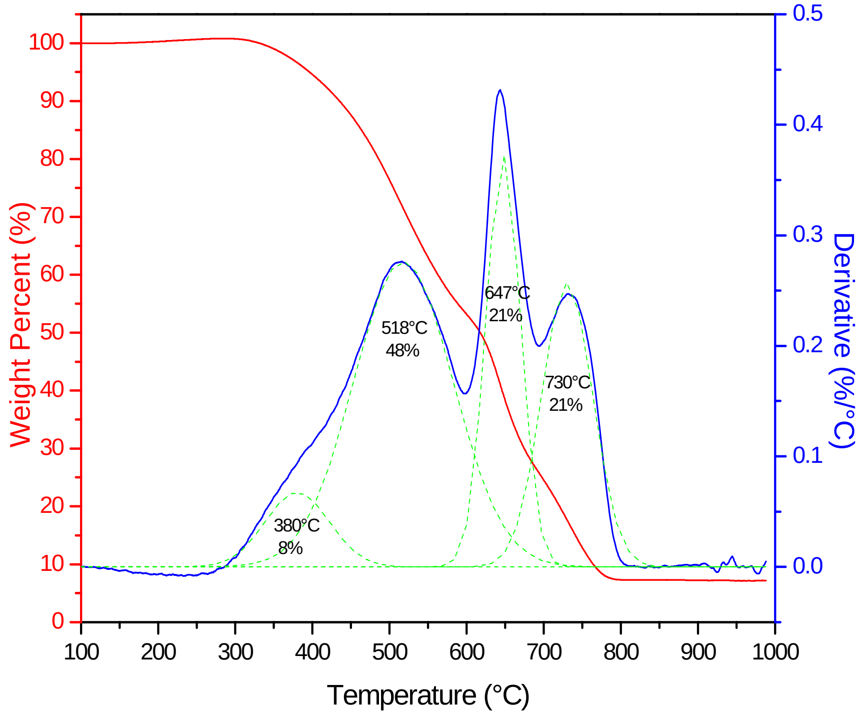


Purified

Arepalli, et al., *Carbon* **42** 1783 (2004)

- Useful for identifying relative changes due to processing
- Purification
  - reduction in metal residue
  - increase in bulk oxidation temperature

TGA/DTG Limitations

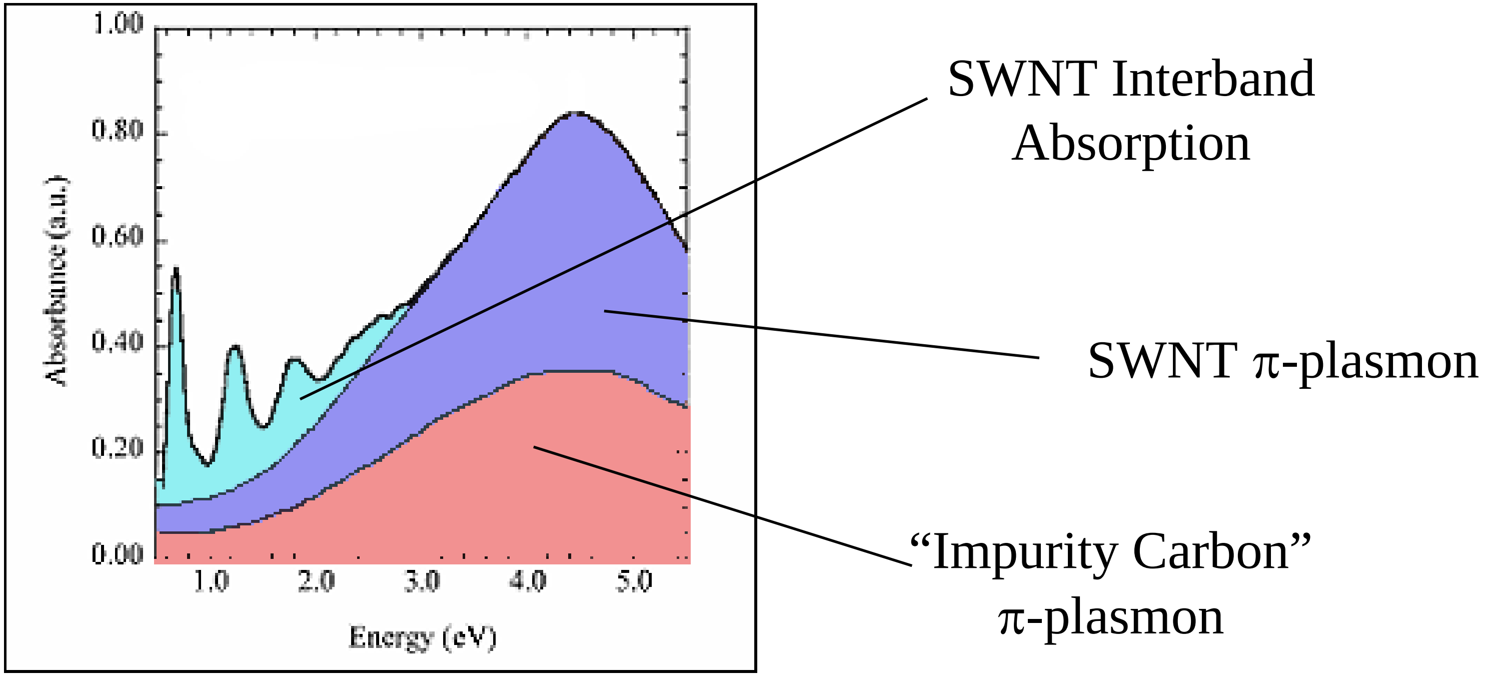


Very difficult to assign individual oxidation events to specific carbon species

- similar oxidation temperatures
- metal catalyzed oxidation
- exothermic effects

Absorption Spectroscopy: UV-Vis-NIR

- Because of their unique electronic structure, SWNT have discrete optical absorptions that do not occur in other graphitic nanocarbons.
- Very useful as a relative purity measurement

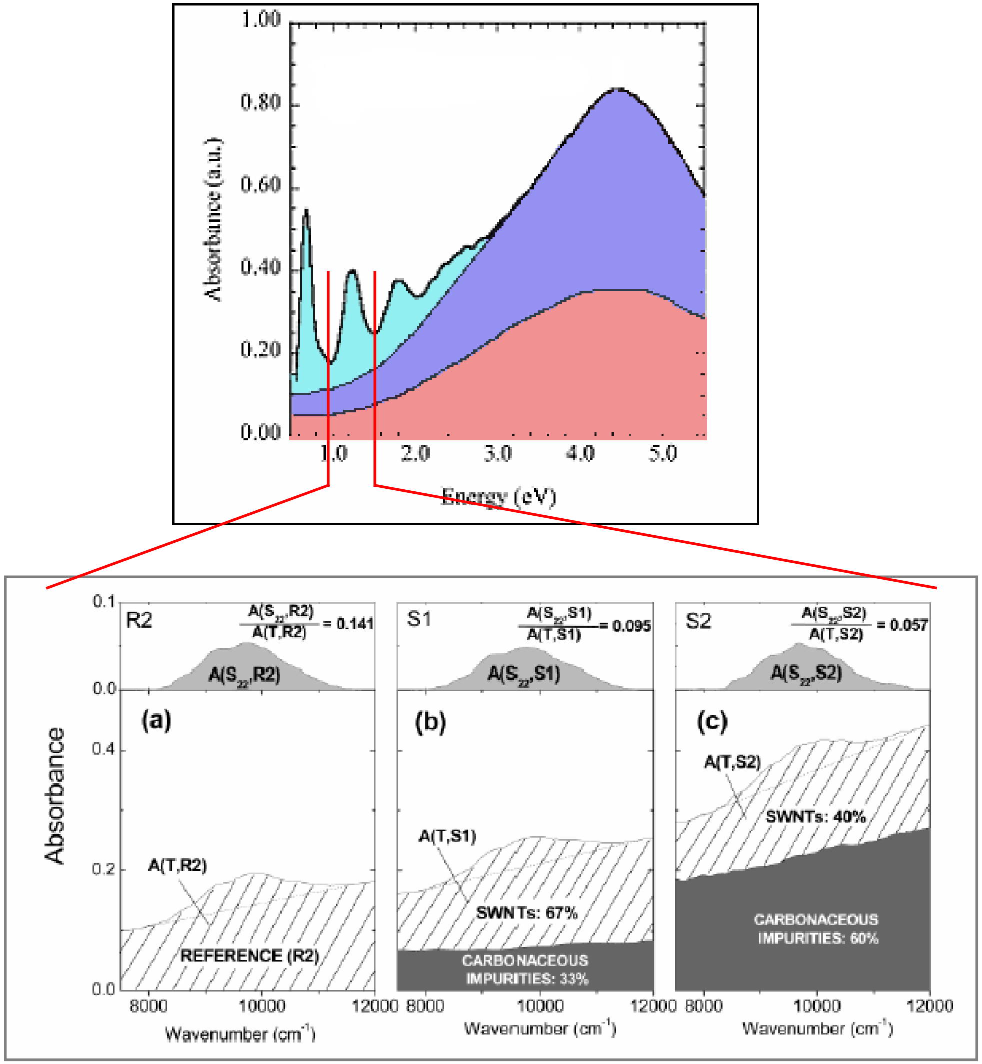


Method

- Beer's Law:

  $$A = \varepsilon CL$$

- Prepare and measure a reference sample for comparison
- Ratio an unknown against the reference to determine relative purity



Itkis, et al., *JACS* **127** 3439 (2005)

UV-Vis-NIR Limitations

- Absolute purity measurement requires a 100% pure reference
- Requires a different reference for EACH production method & diameter distribution
- SWNT from some sources do not easily form stable dispersions
- Some evidence that SWNT and impurities have different dispersion stabilities
- SWNT from some sources have broad diameter distributions – excessive band overlap

Challenges facing SWNT characterization

- No single technique can give a complete description of a SWNT sample
- Limits to the conclusions that can be drawn from each technique
- Sample preparation and measurement protocol can have a big impact
- Measurements become more useful when compared against a reference
- Difficult to make direct comparisons between SWNT made by different methods

Need for Standards

Establish standards for all characterization techniques

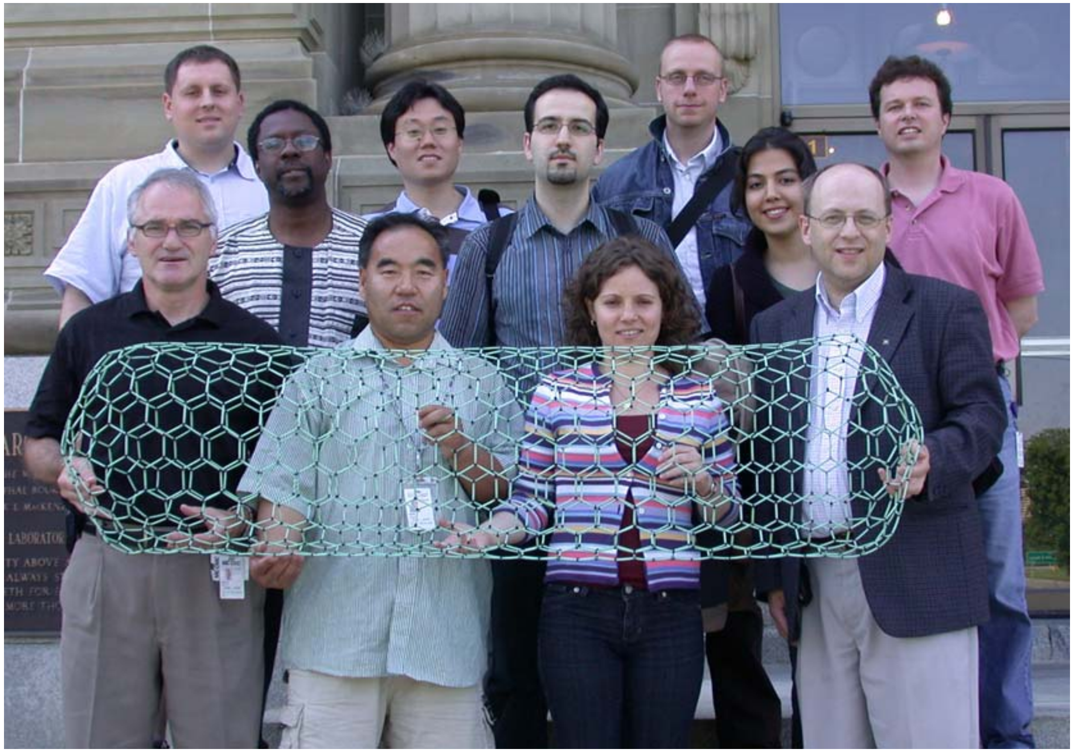
- sample preparation
- measurement conditions and protocol
- data analysis
- reference materials
- interpretation

Direct benefits:

- reduce confusion due to conflicting information
- allow objective comparison of different SWNT samples
- favor the adoption of SWNT into commercial applications

Thank You

- Our SWNT Team



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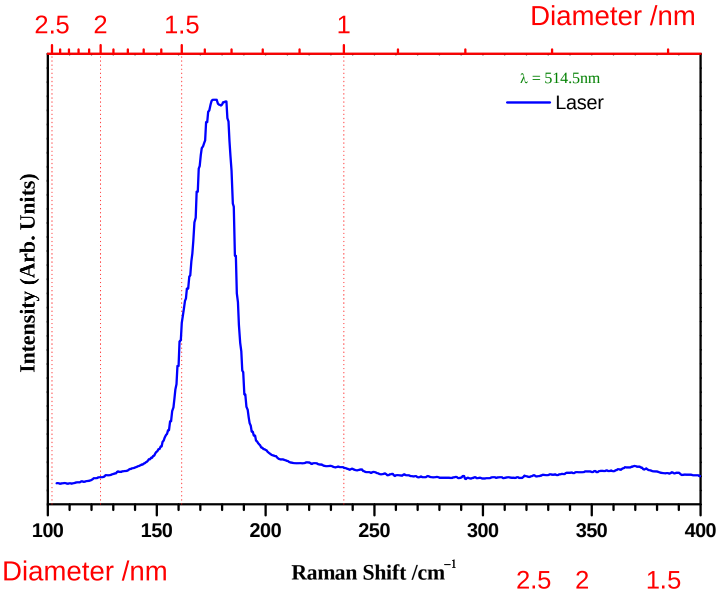
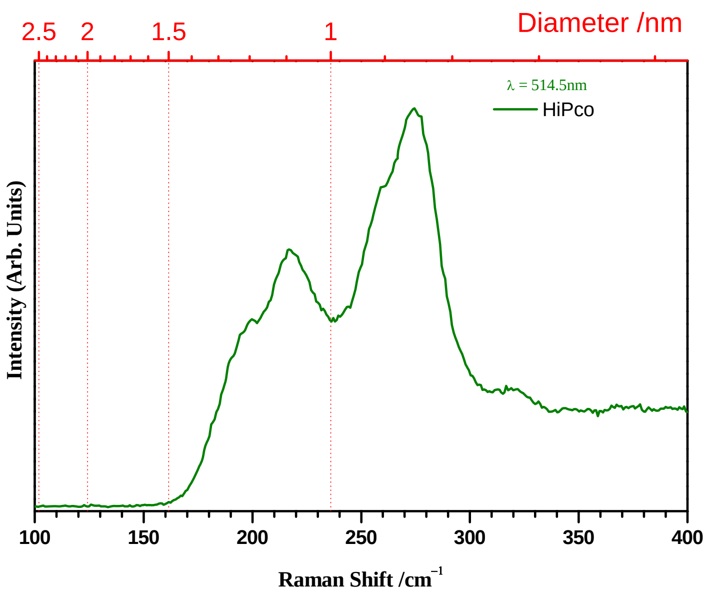
Diameter: The RBM

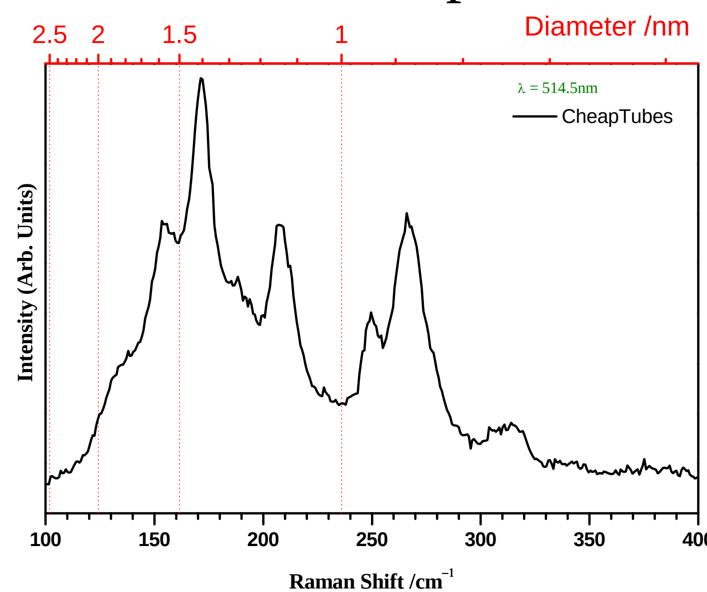
NRC-Laser SWNT



HiPco

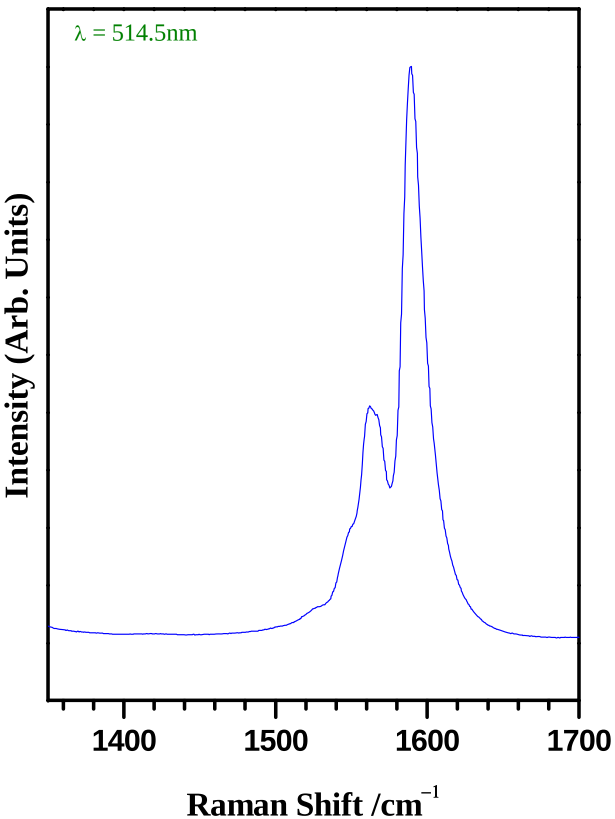


CheapTubes.com



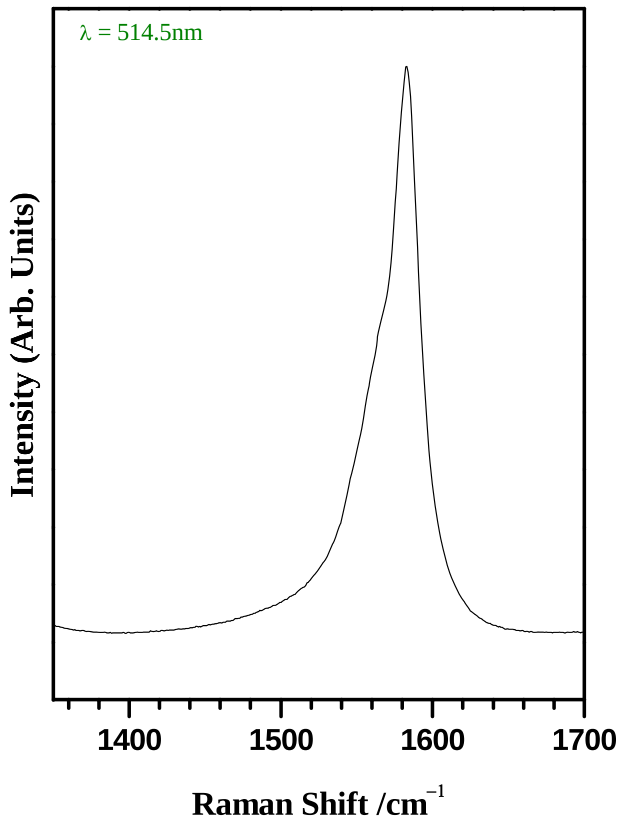
Metal-Semiconductor: The G-band

Laser



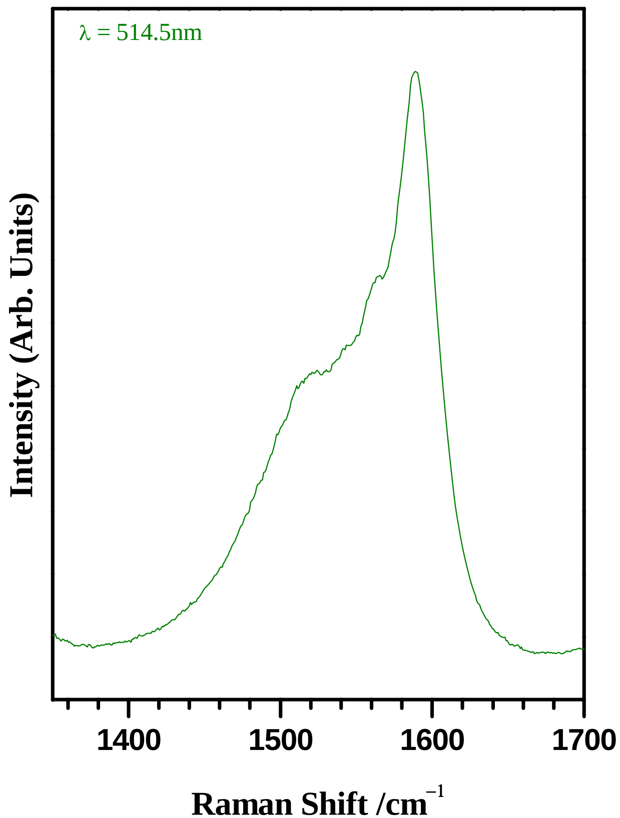
Probing: Semiconducting

CheapTubes.com



Both

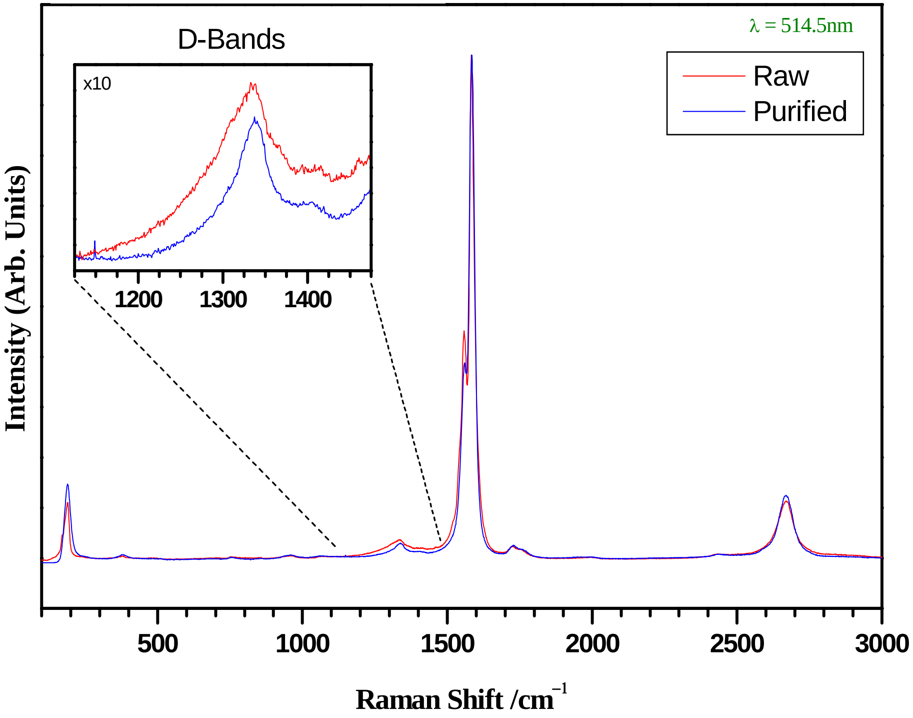
HiPco



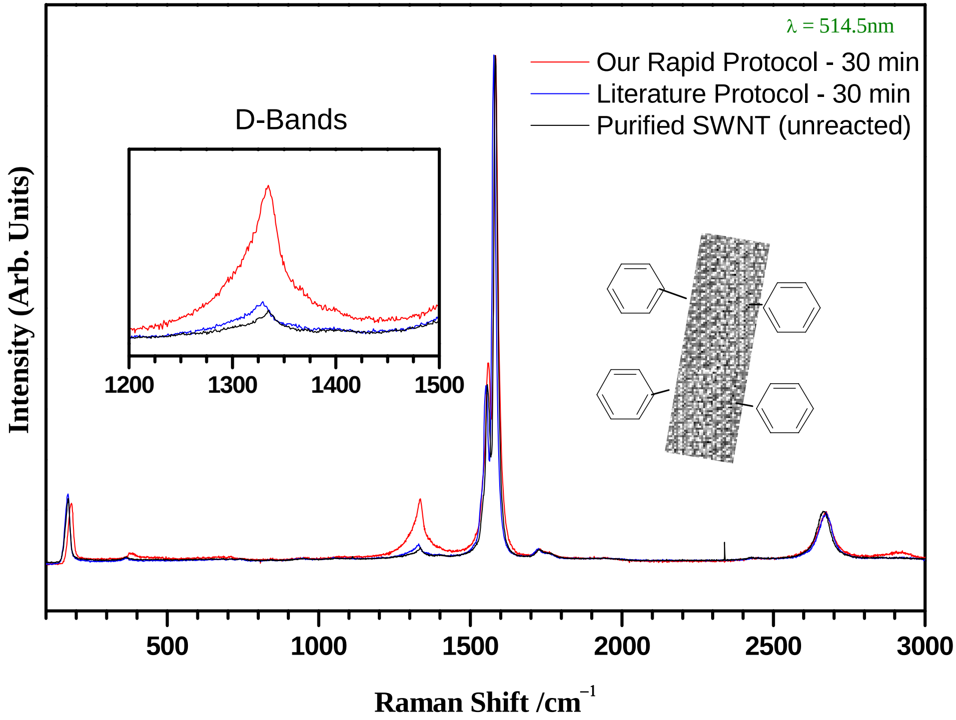
Metallic

Purity & Defects: The D-band

Purity Assessment



Functionalization Assessment



The intensity and width of the D-band are indicators of the levels of impurities and/or tube defects in the sample.