Characterization of Length, Diameter, and Metal Content of HiPco Tubes

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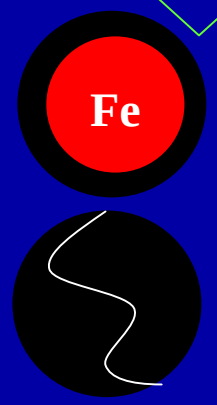
Purification of SWNTs

- Current Methods
  - Acid Oxidation
  - Gas Oxidation
  - Filtration
  - Chromatography
  - Mechanical Purification
  - Selective Microwave Heating
  - Organic Functionalization
- Disadvantages
  - Low yield
  - High metal content
  - Sidewall damage
  - Scalability

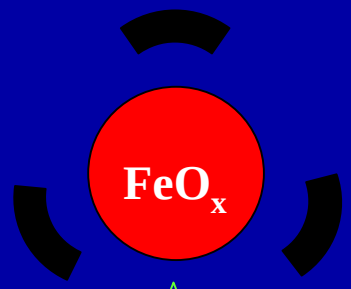
Purification Mechanism

Carbon coating prevents dissolution with HCl



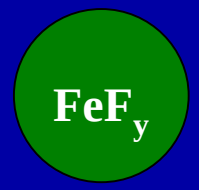
O_2

Crack carbon shell



$C_2H_2F_4$ or SF_6

Catalyst Deactivation



$+ \quad CO_2$

Seams on the carbon shells

Fe_2O_3 has catalytic effects on nanotube oxidation . It's existence decreases the cleaning carbon yield.

The fluorine-containing gas converts the metal oxide into metal fluoride and deactivates the metal catalyst.

Consolidation of Raw Tubes

Raw tubes collected from HiPco

Spray IPA to consolidate the fluffy raw tubes

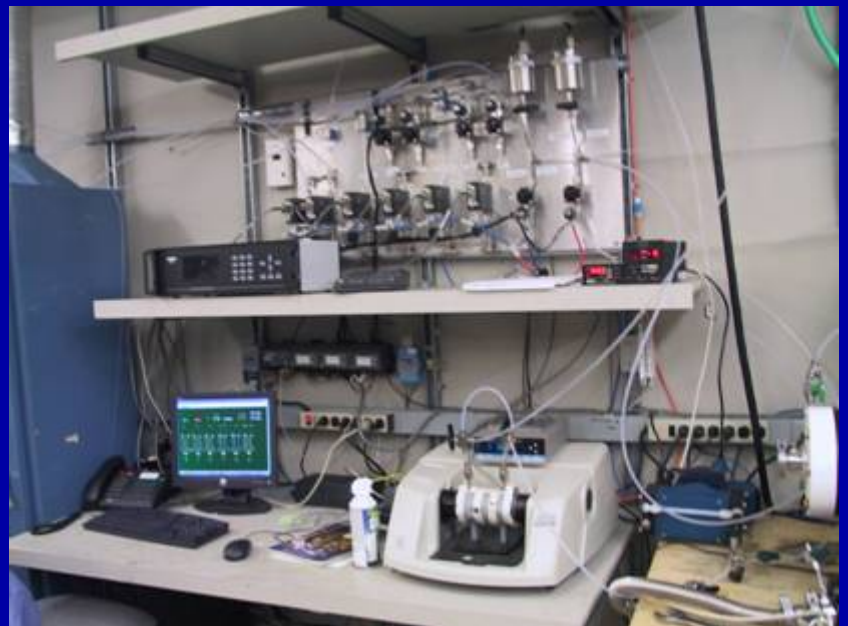
Purification Cartridge

Add tubes into the purification cartridge

- Gas flow through thin layer of tubes yields uniform temperatures
  - Minimizes hot spots
- Spacers fill void areas
  - Standardize layer thickness for each purification

Controlled Oxidation

- Computer controlled step-wise oxidation
  - 150 – 325 ºC
  - 25 ºC increments
  - 60 min oxidation
  - 30 min deactivation



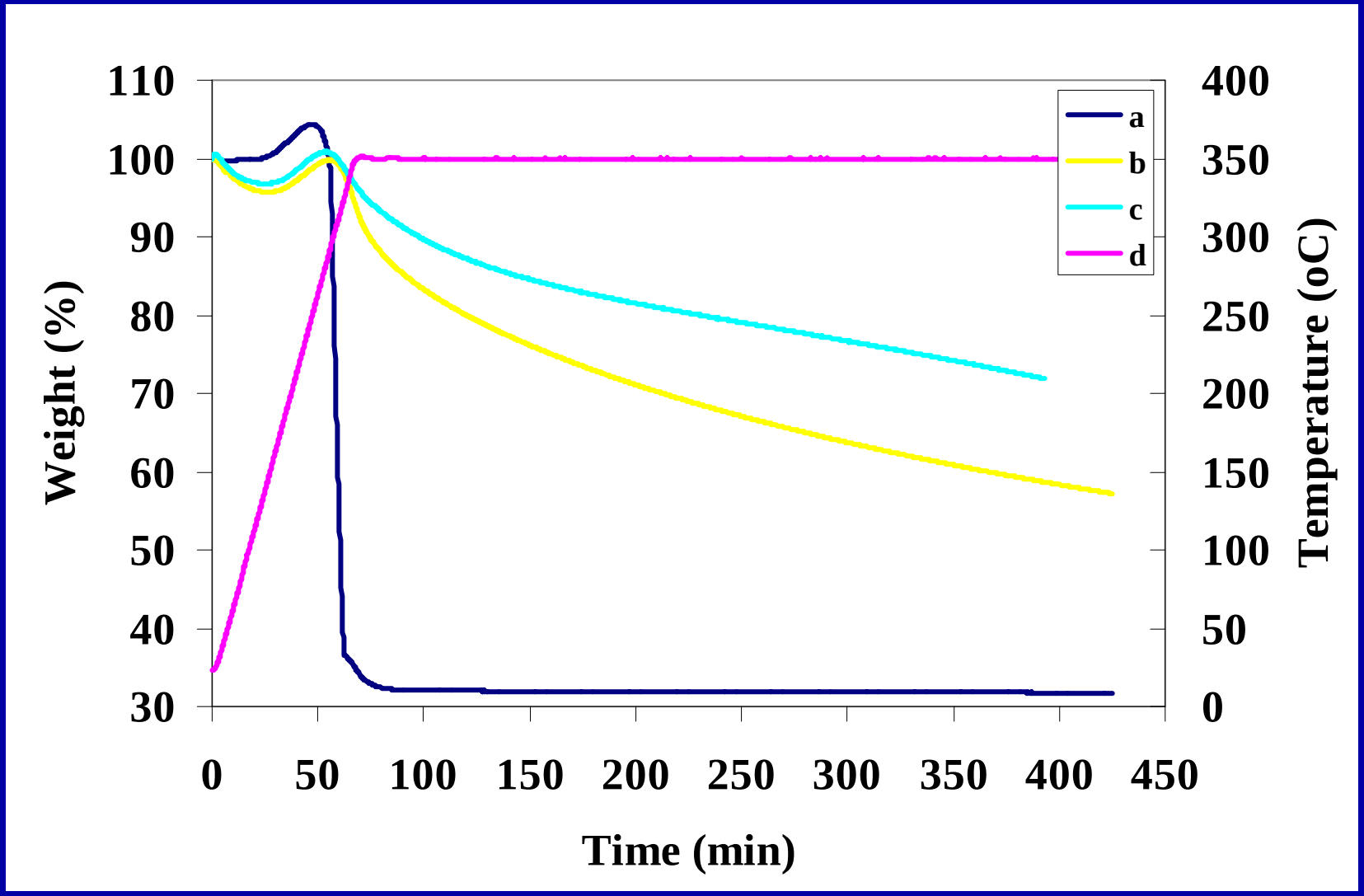
Metal Removal

6M HCl Soxhlet Extraction

Hexane Extraction

Buckypearl

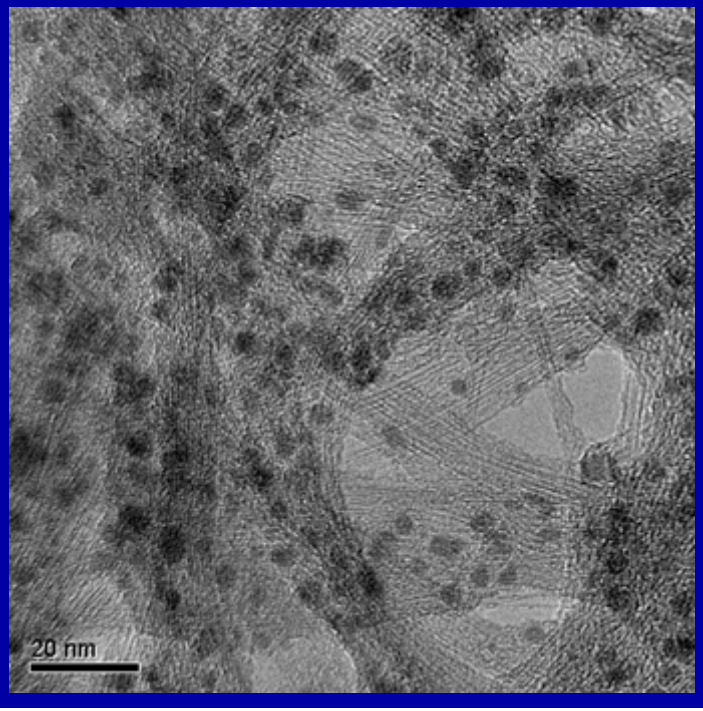
Deactivation of Catalyst

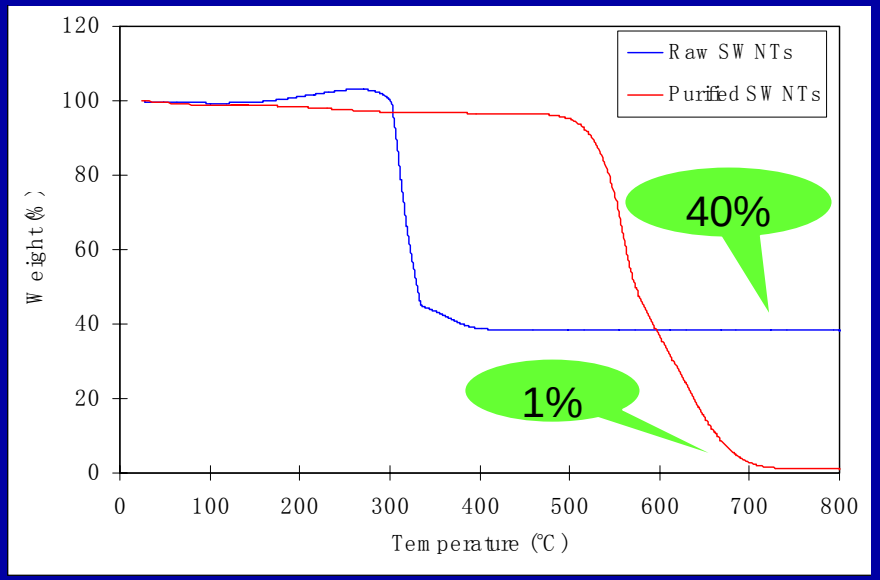


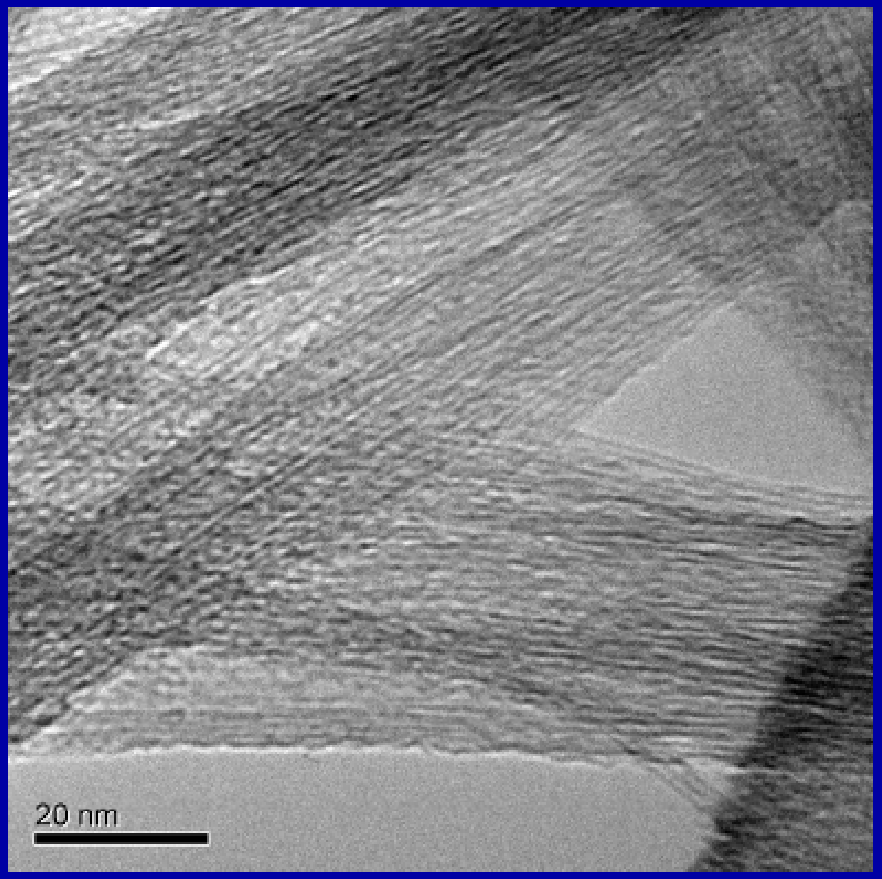
(a) 20%O_2, (b) 20%O_2 and 5% $C_2H_2F_4$, (c) 20%O_2 and 5% SF_6, (d) temperature.

Purity

Raw tubes

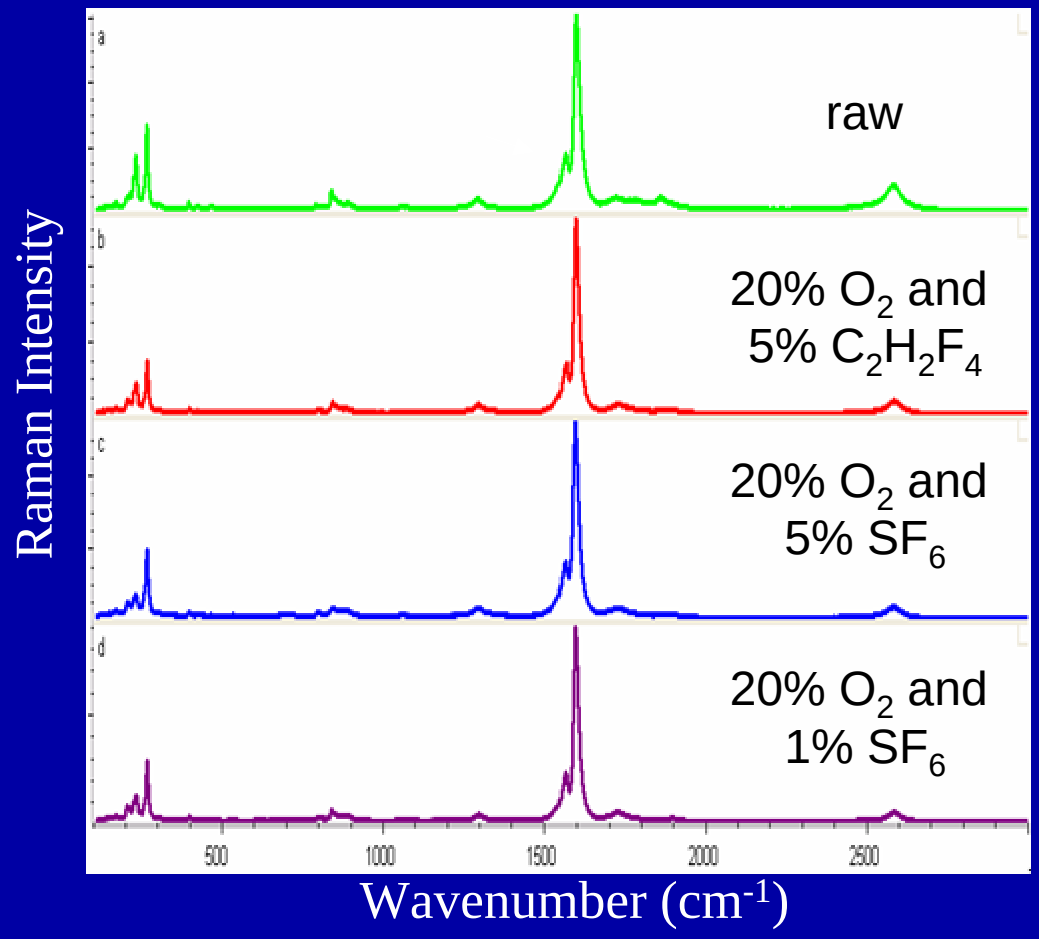




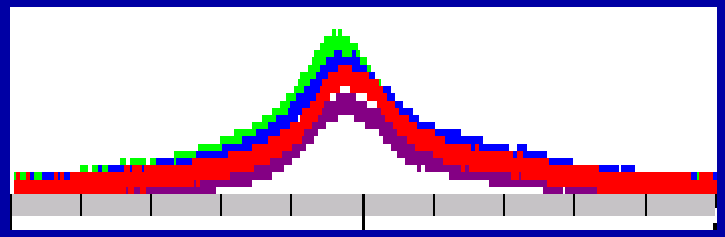


Purified tubes

Sidewall Damage



D-band

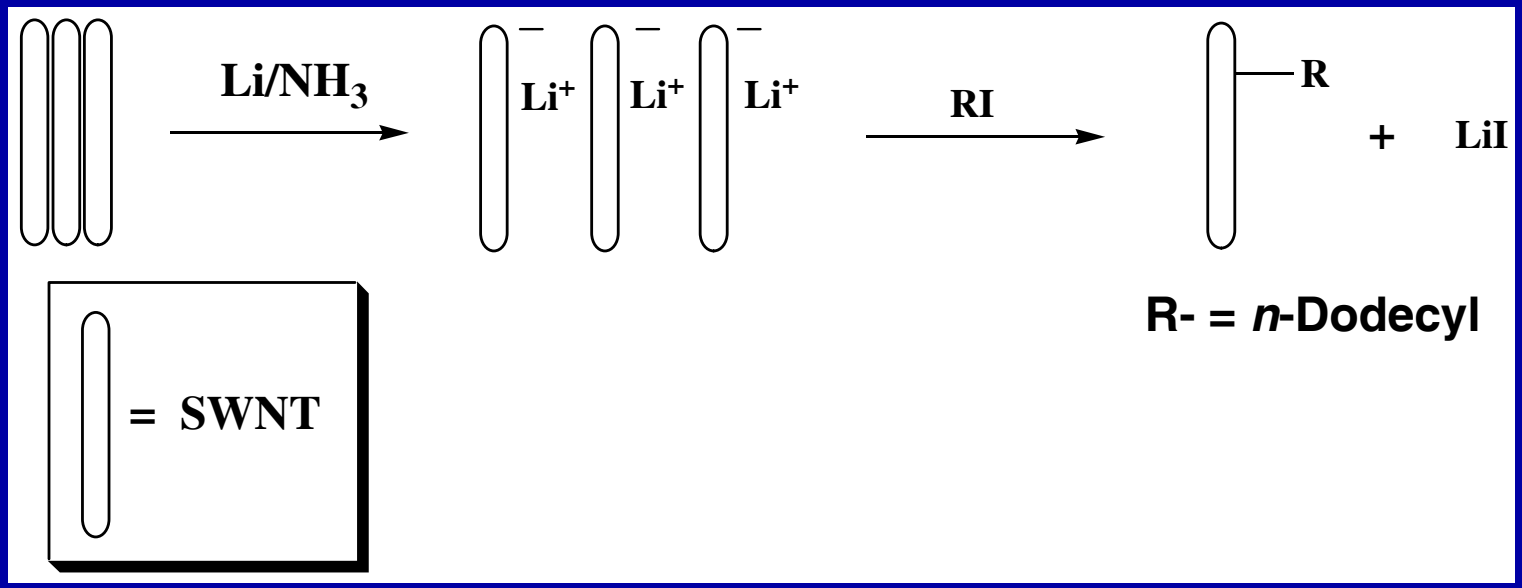


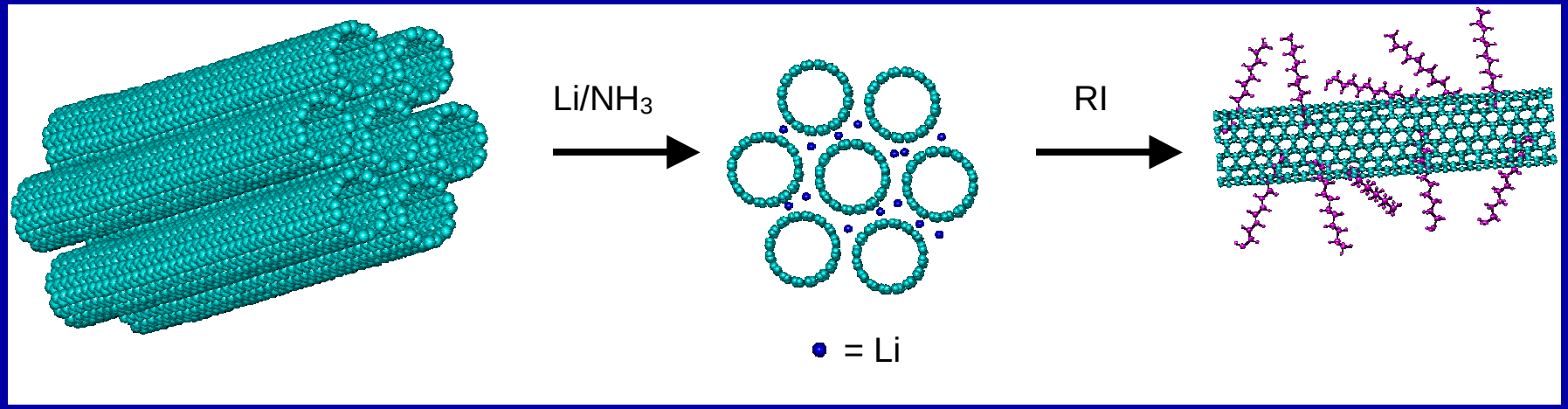
- Disorder band decreases after purification

Nanotube Length Measurements

- Important for understanding growth and cutting processes
- In-situ techniques only give an average length and no information about distribution
- Direct imaging techniques are tedious but give more information
  - Limited by the suspension of individual nanotubes
  - Tedious nature of measuring 1000+ nanotubes
- Many functionalization routes developed
  - Few give significant degree of individual tubes
- Surfactant solutions and centrifugation yield significant amount of individuals
  - Removal of solid material can alter the measured population

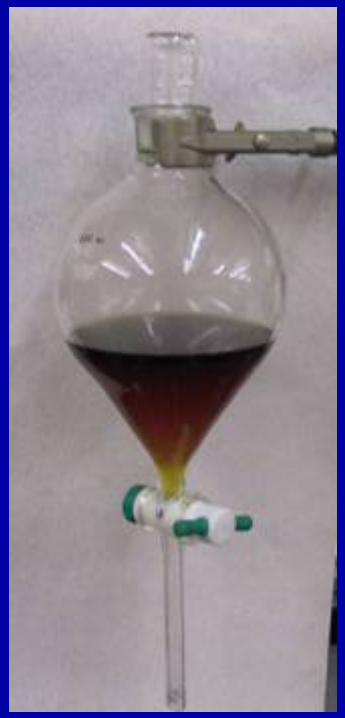
Reductive Alkylation (Li/NH_3)



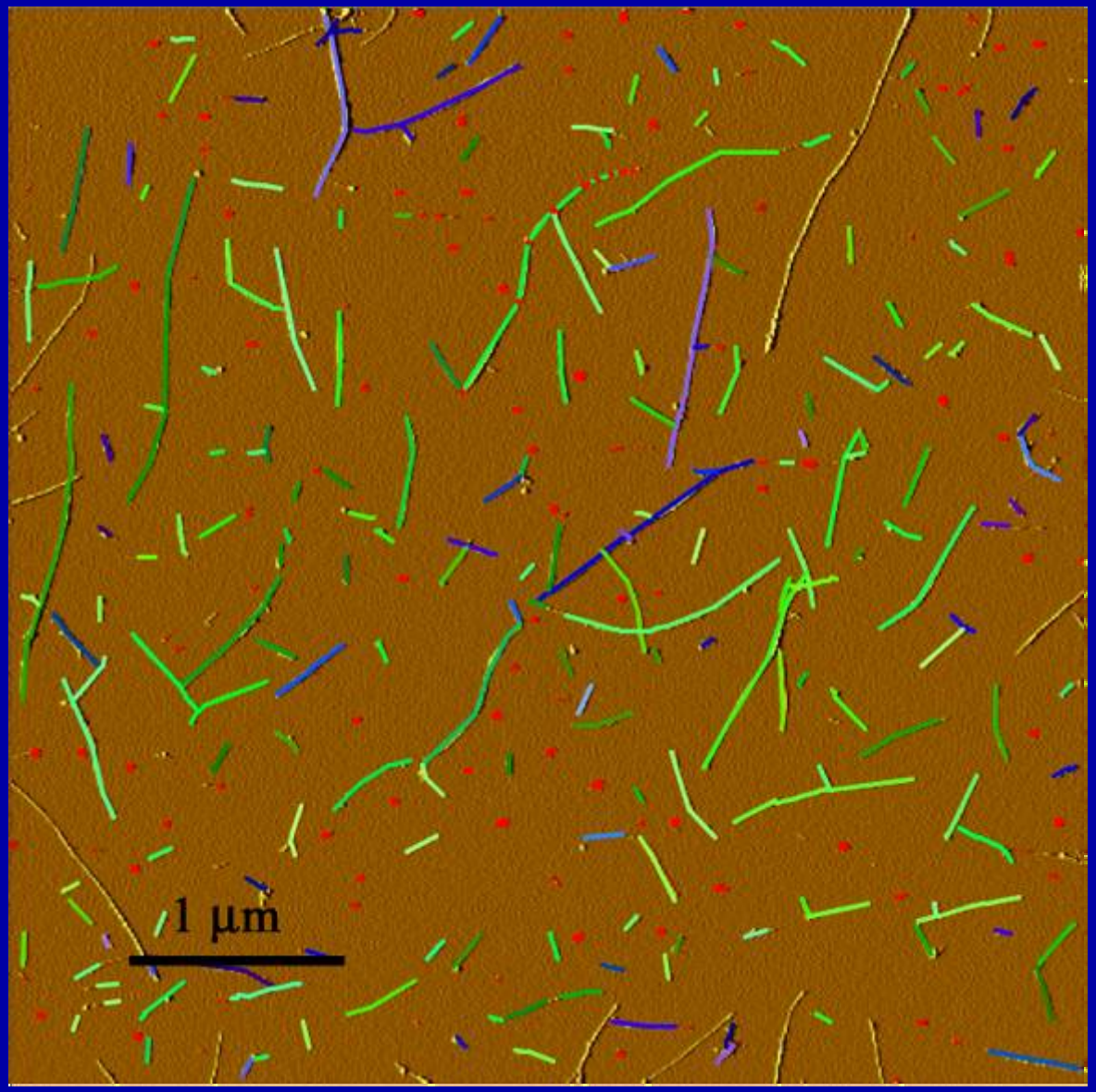


Reaction Setup

- Simple reaction setup
- Easy work-up
- Suspensions in $CHCl_3$
- AFM on mica
- 80 – 90% individuals

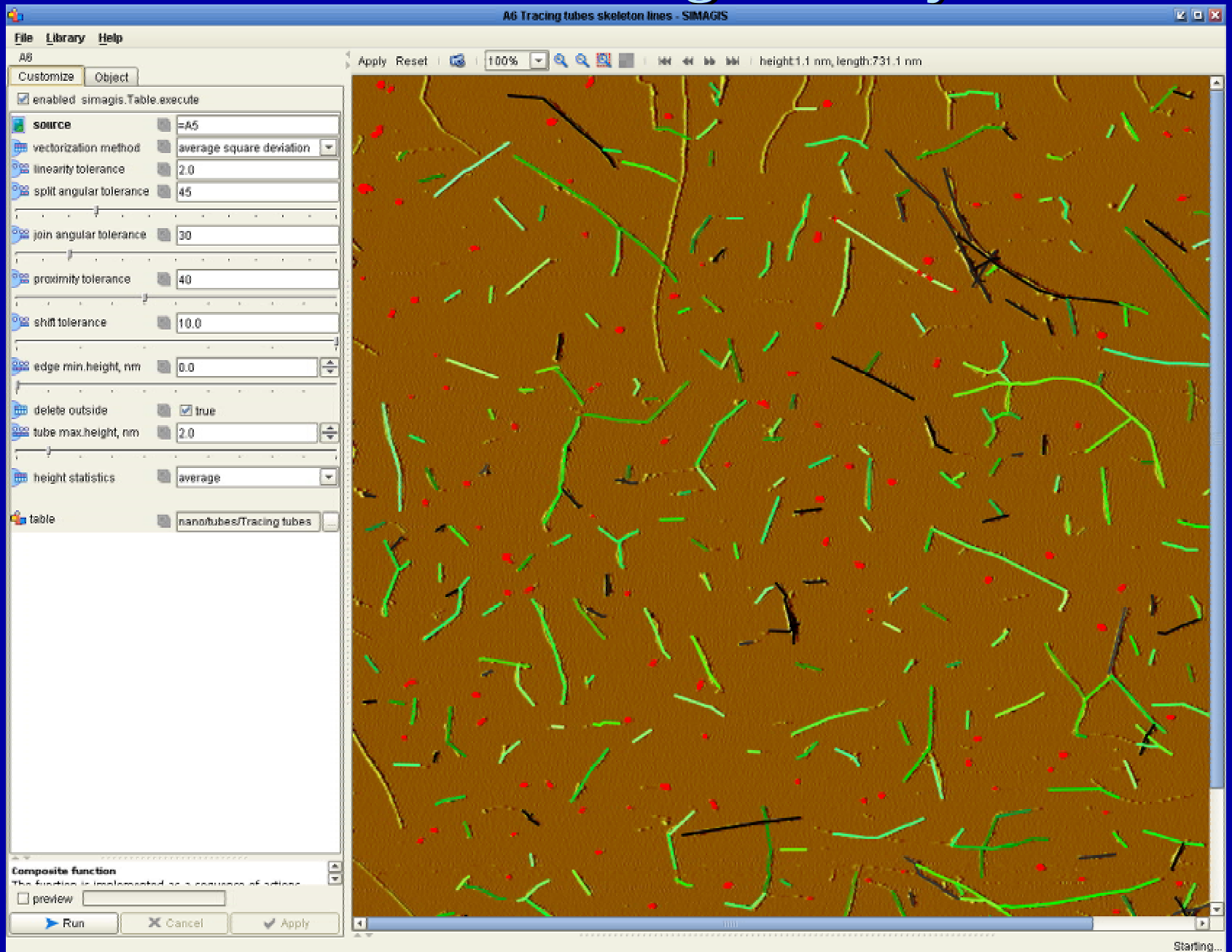


Automated Nanotube Length Analysis



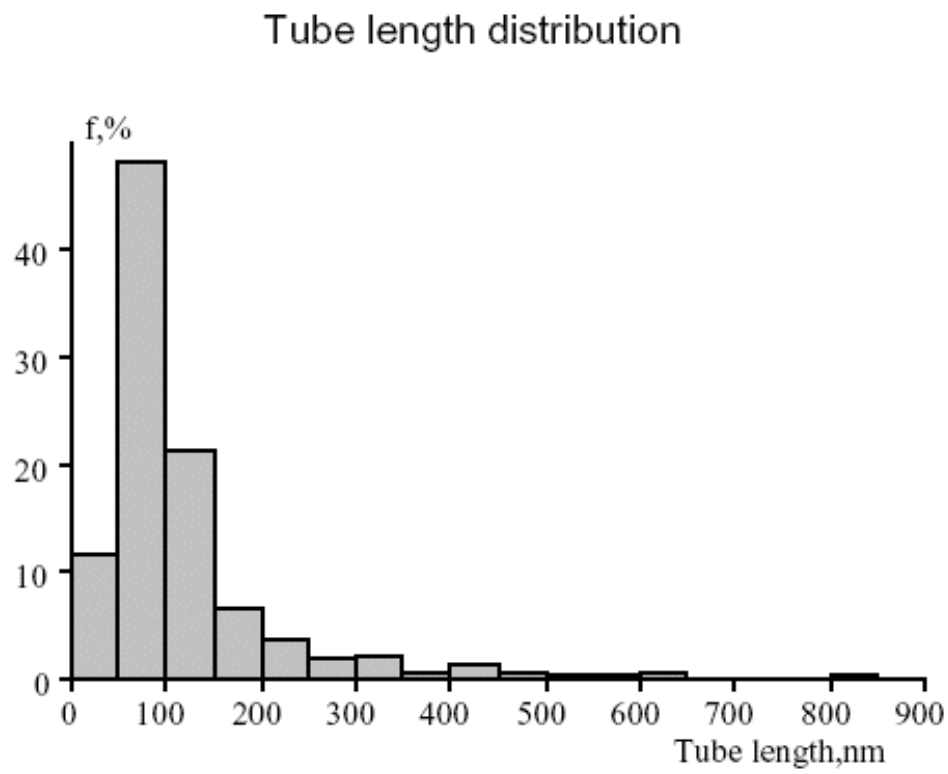
- Fast length measurements
  - < 1 min / image
- Differentiate heights
  - Tubes (green)
  - Ropes (blue)
- Statistics
  - Lengths
  - Heights

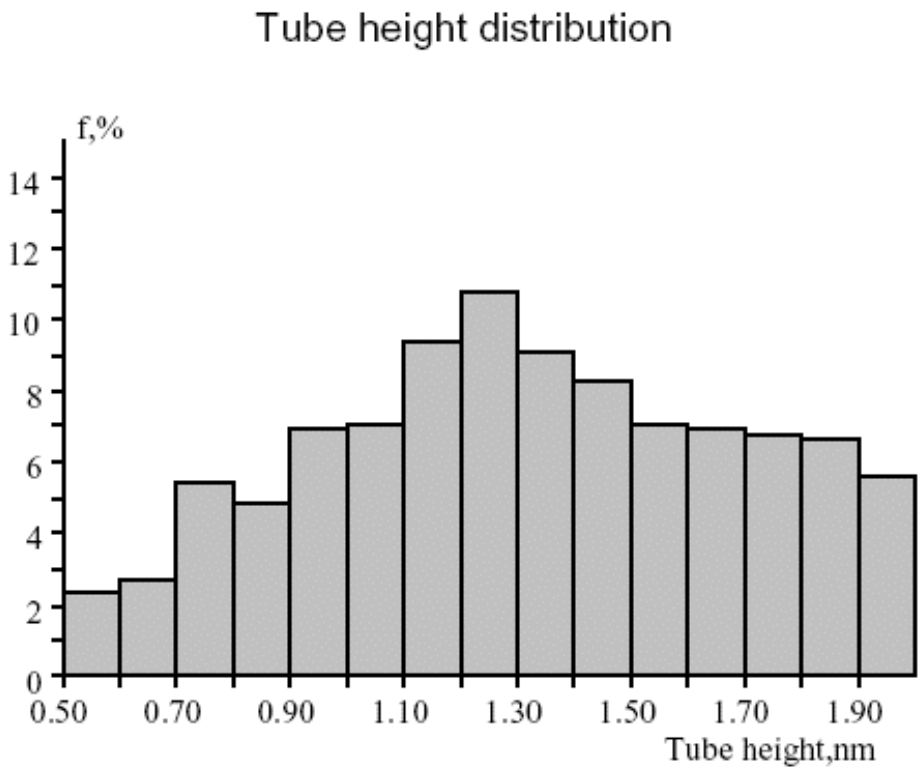
SIMAGIS Nanotube Length Analysis Module



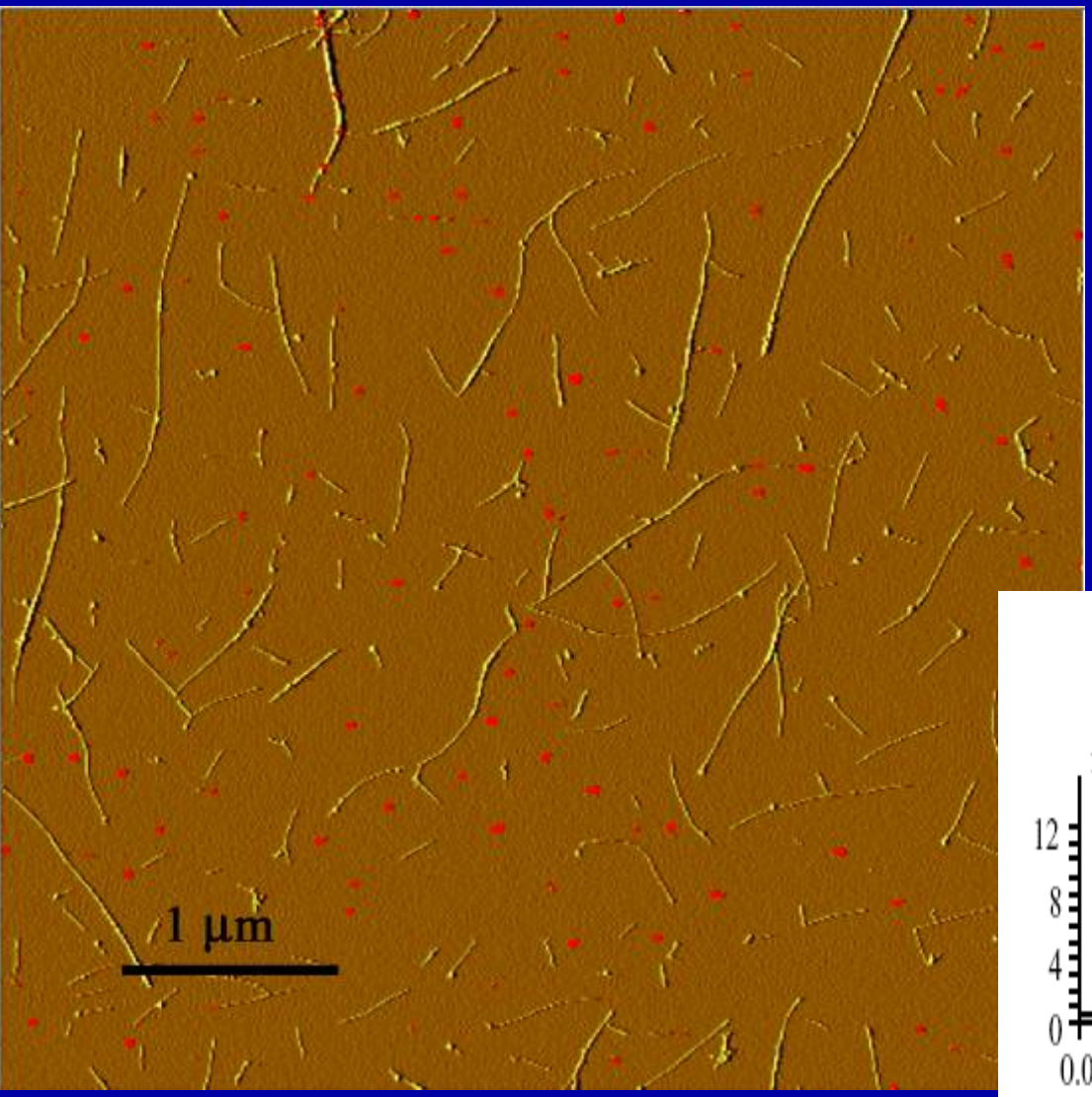
Length and Height Distributions

- Combination of multiple images allows measurement of 1000+ tubes

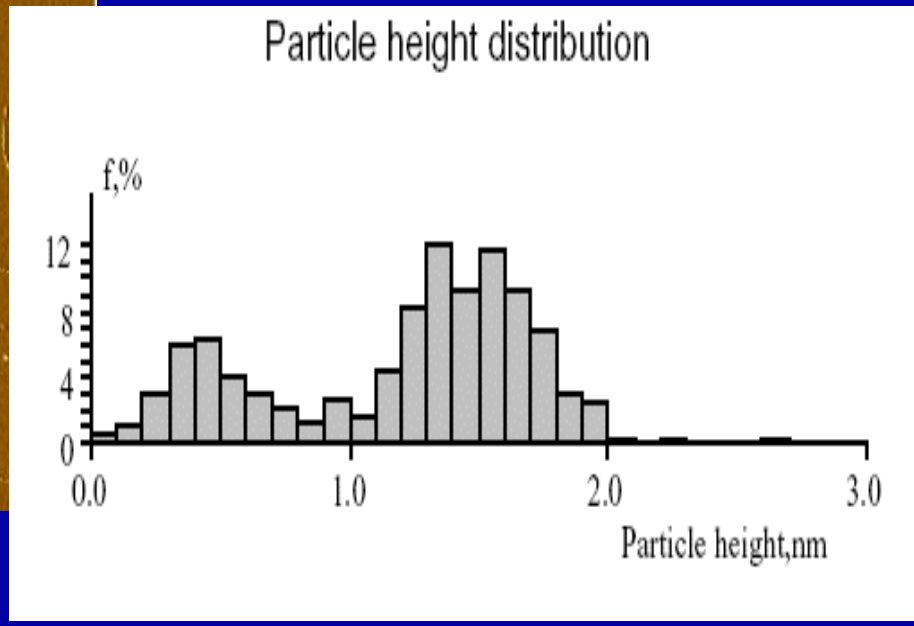




Particle Analysis



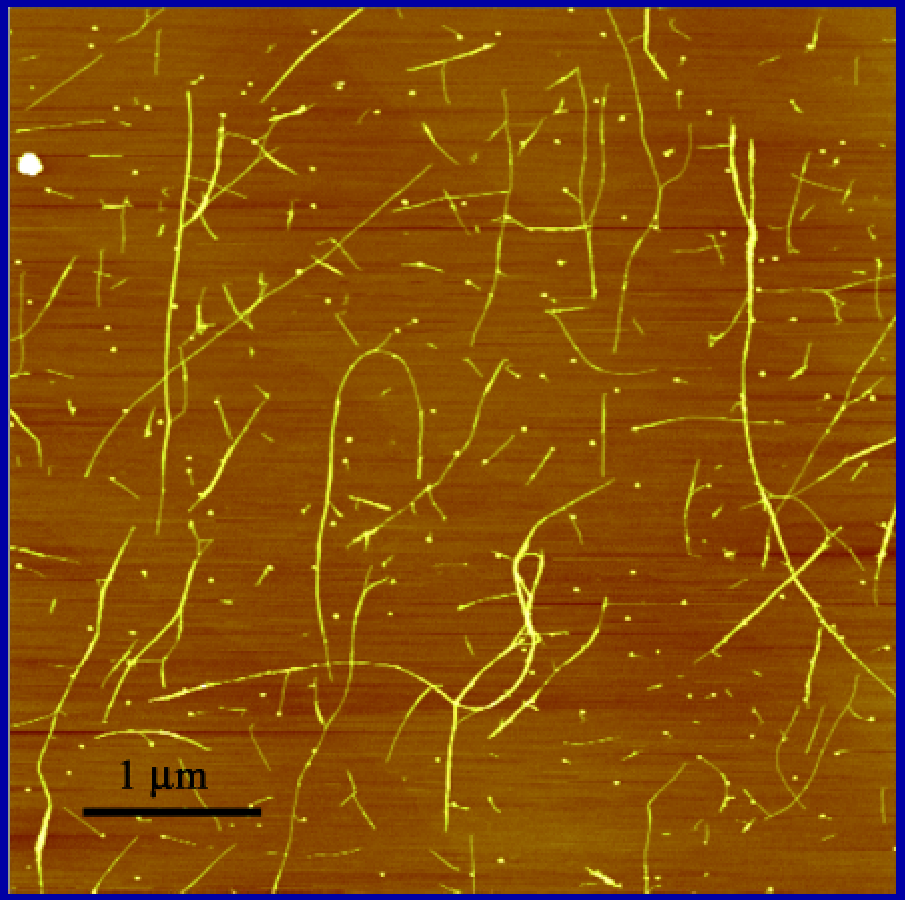
- Diameter distributions of metal catalysts or fullerenes



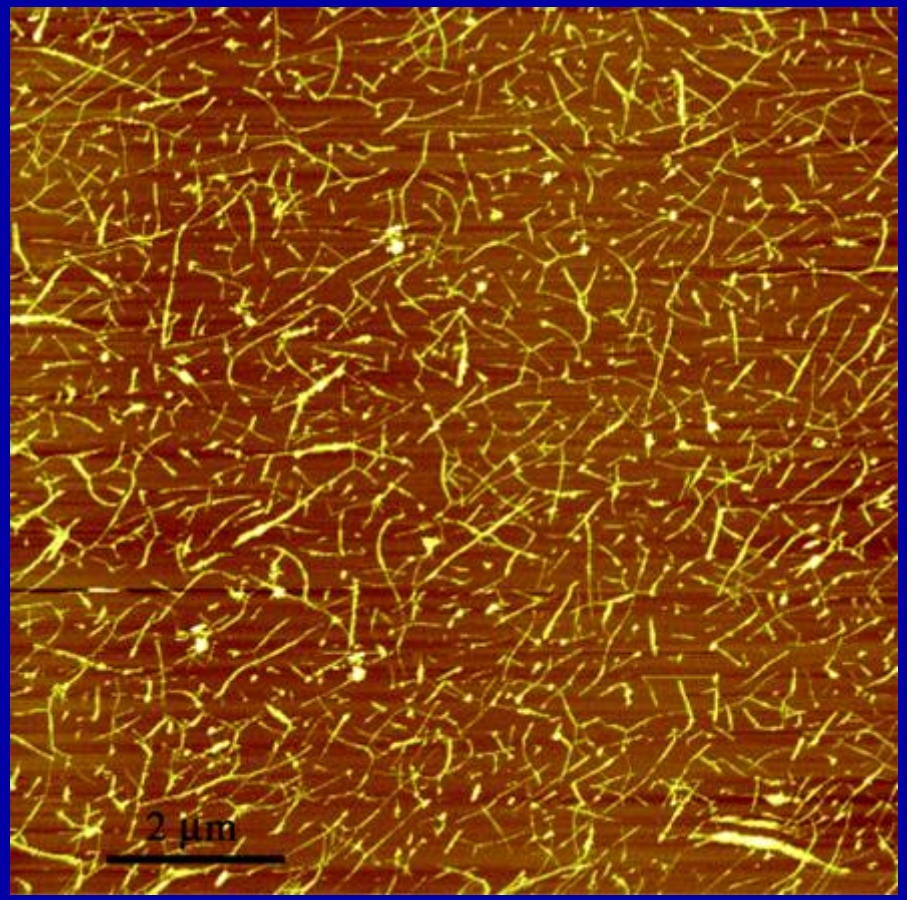
Minimizing User Intervention

- Image quality important
- Ideal surface coverage

Moderate

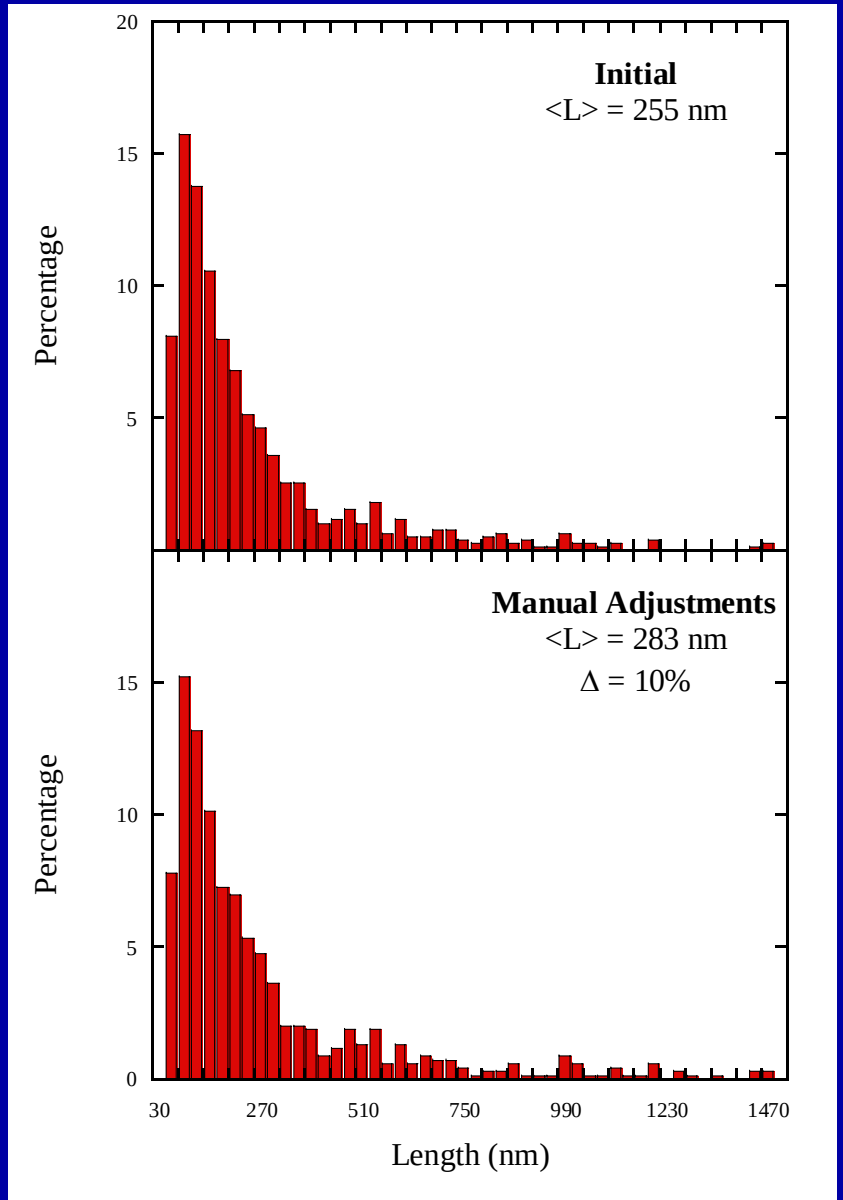


High

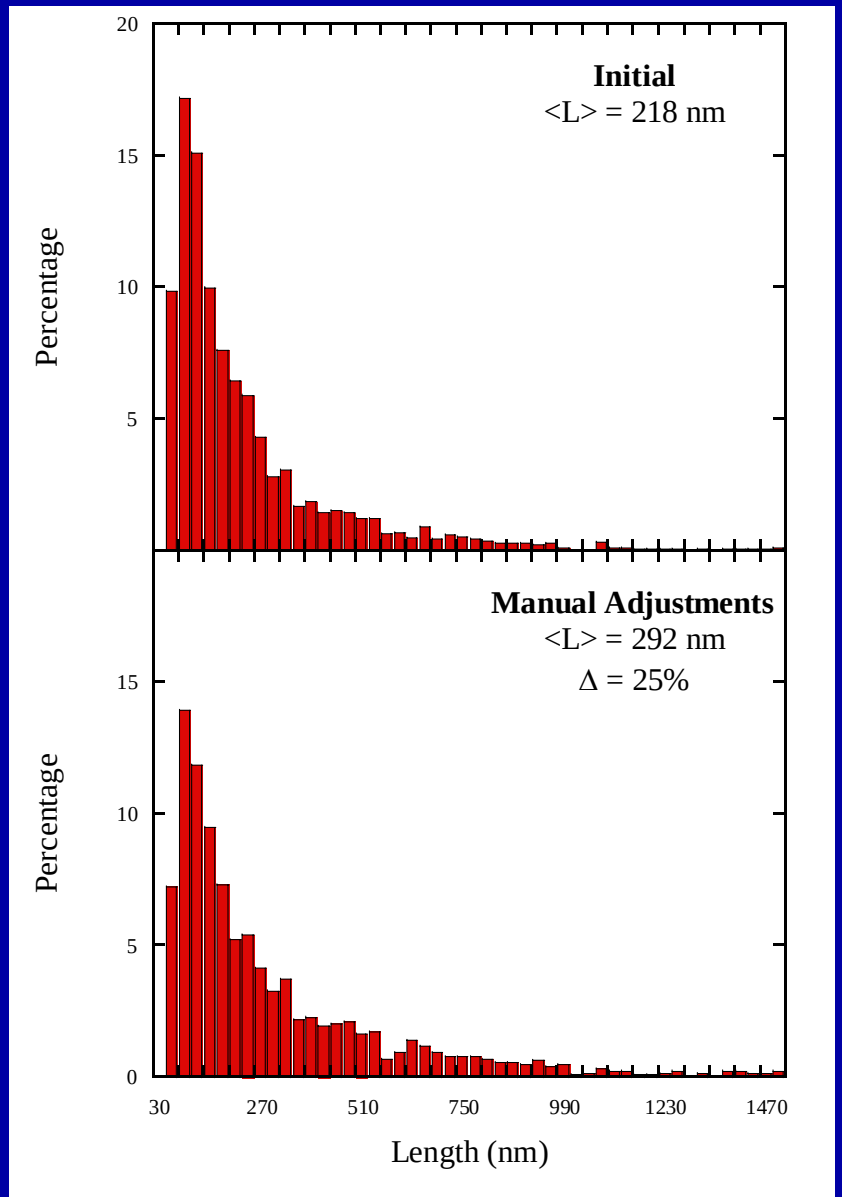


Effect of Surface Coverage

Moderate



High



Obtaining Diameters of SWNTs

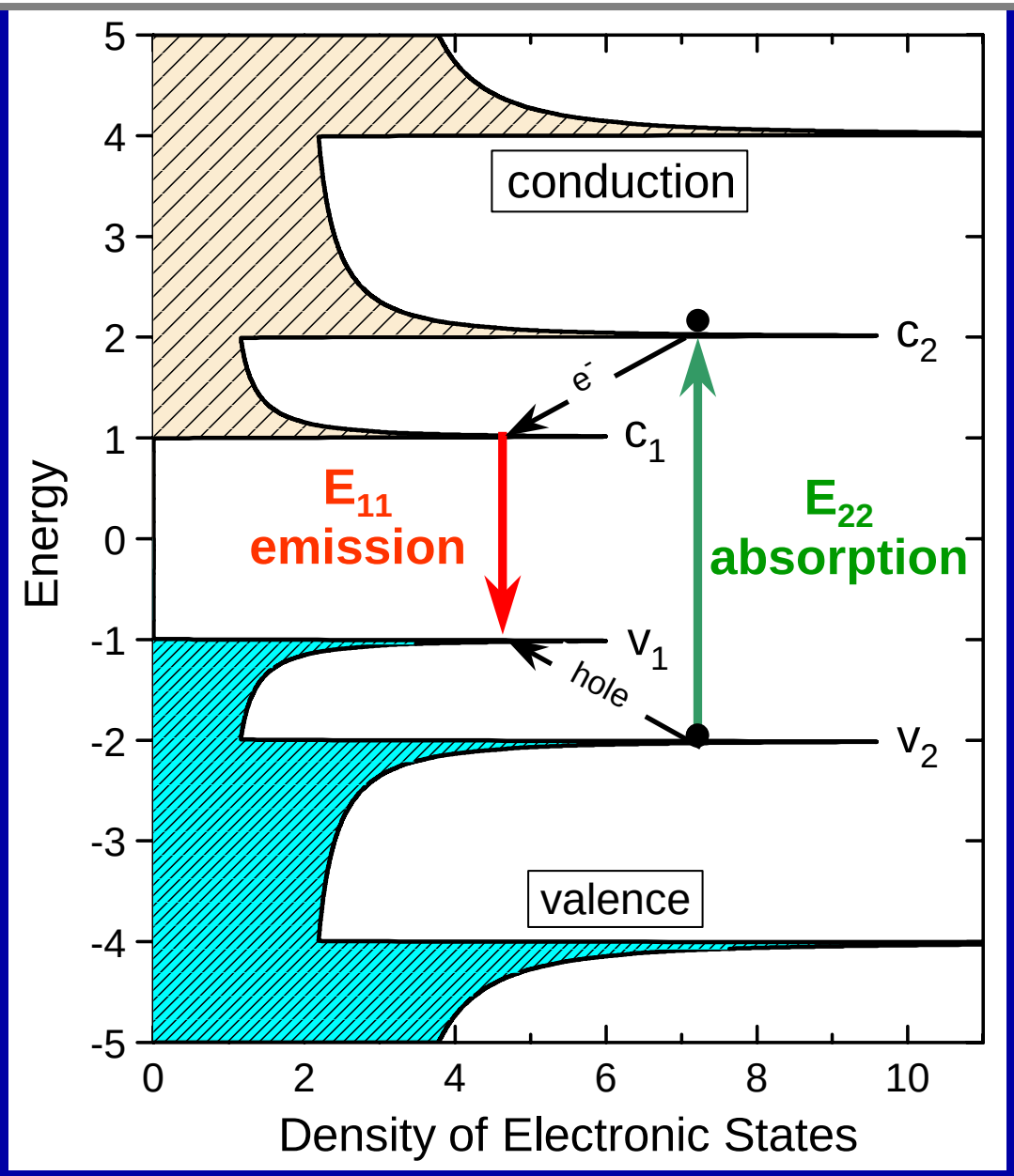
Strategy

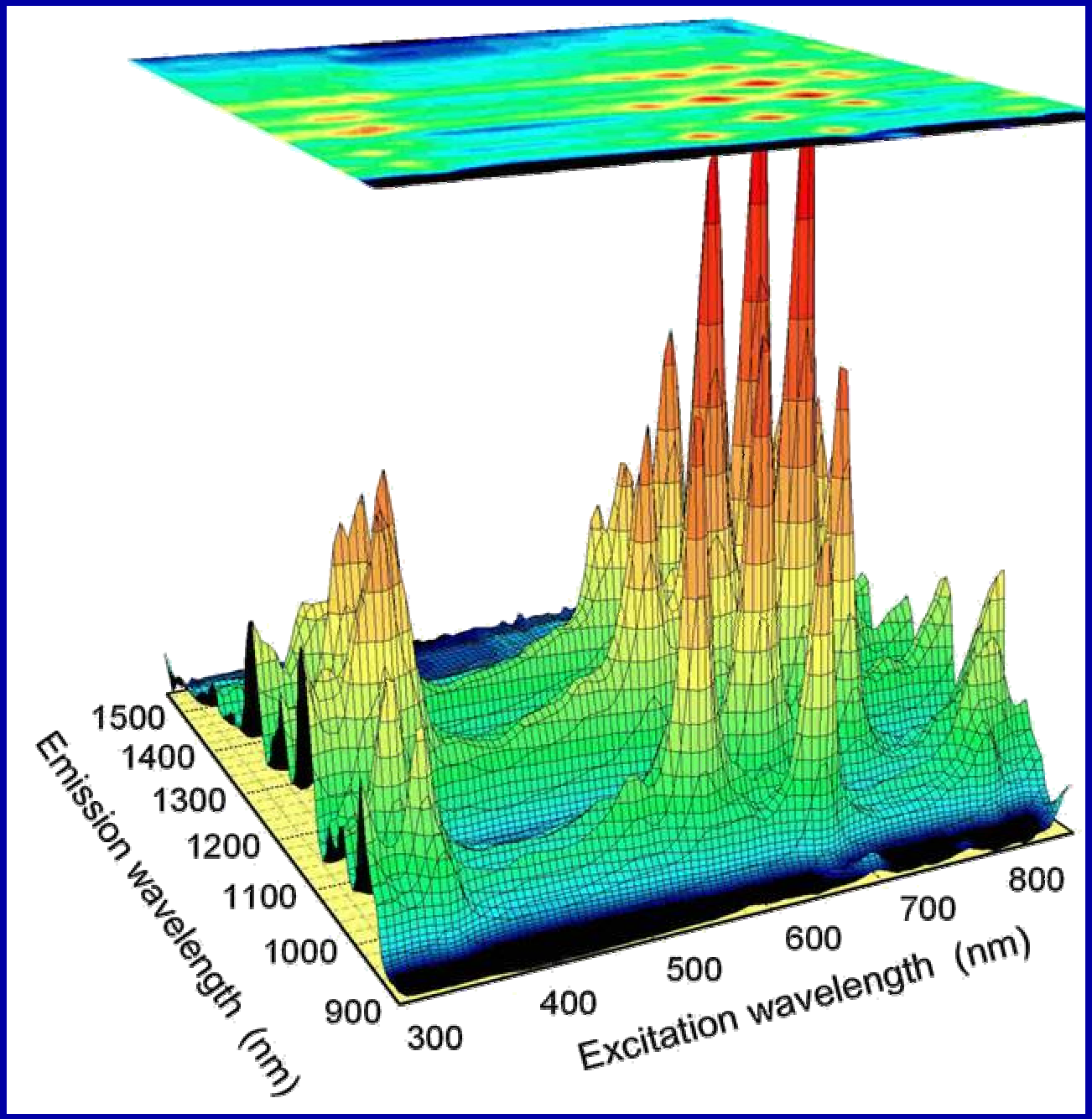
- non-destructive
- reveals composition at (*n*,*m*) level
- quick results
- minimal sample preparation
- works with small bulk samples
- performed by a non-specialist

Fluorimetry

- each semiconducting SWNT species emits at a characteristic near-IR wavelength
- analyze a sample's emission spectrum to deduce detailed composition
- prototype instrument developed at Rice for NASA Johnson Space Center

Electronic States of Semiconducting SWNT



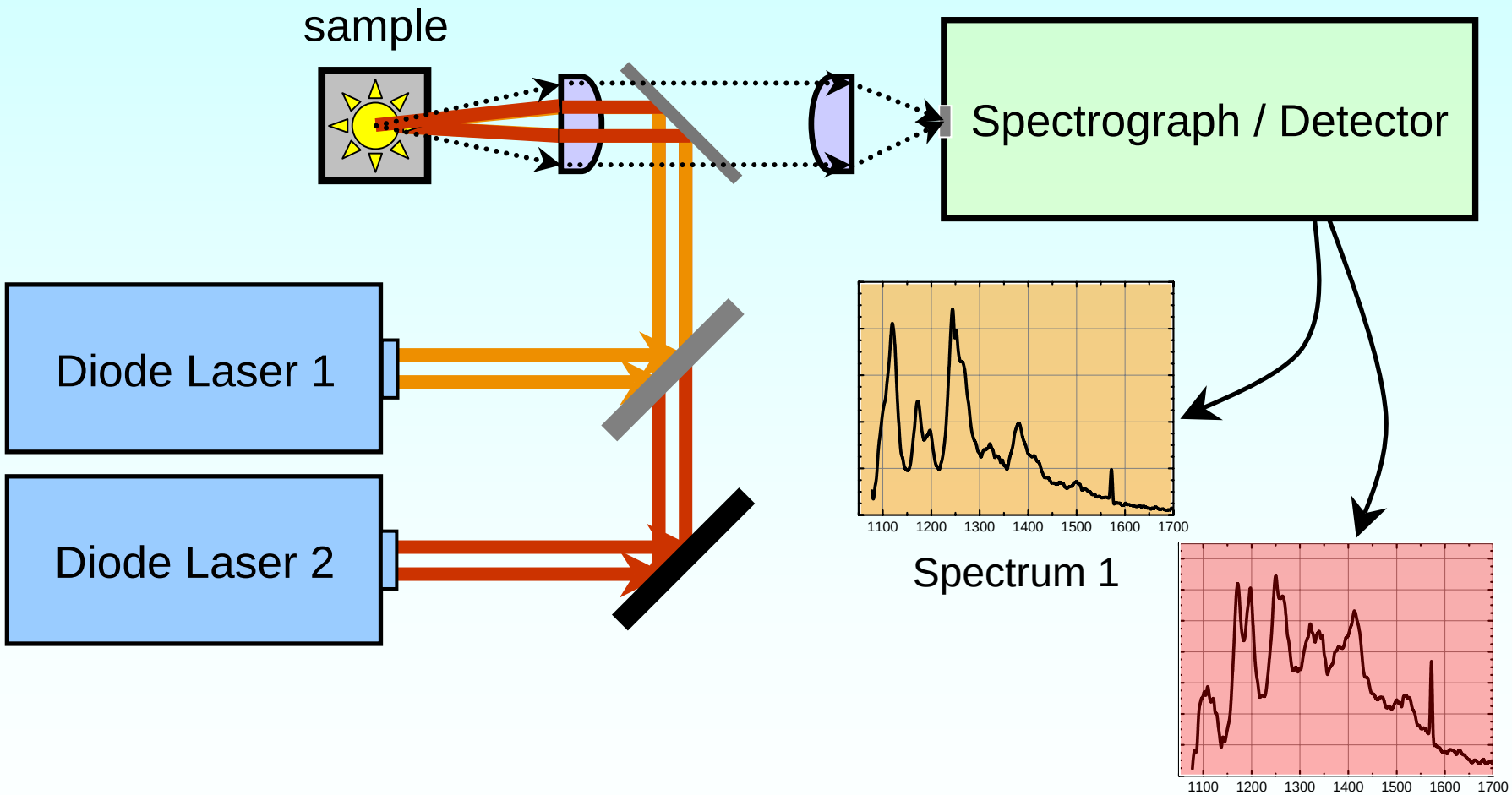

1500
1400
1300
1200
1100
1000
900
Emission wavelength (nm)
300
400
500
600
700
800
Excitation wavelength (nm)

Strategy for Efficient Analysis

- Excite at selected, fixed wavelength(s)
- Capture emission spectrum with a multichannel detector
- Analyze emission spectrum with custom software incorporating SWNT spectral assignments

Fluorimetric Analyzer Prototype

Operation of the *NanoSpectralyzer*



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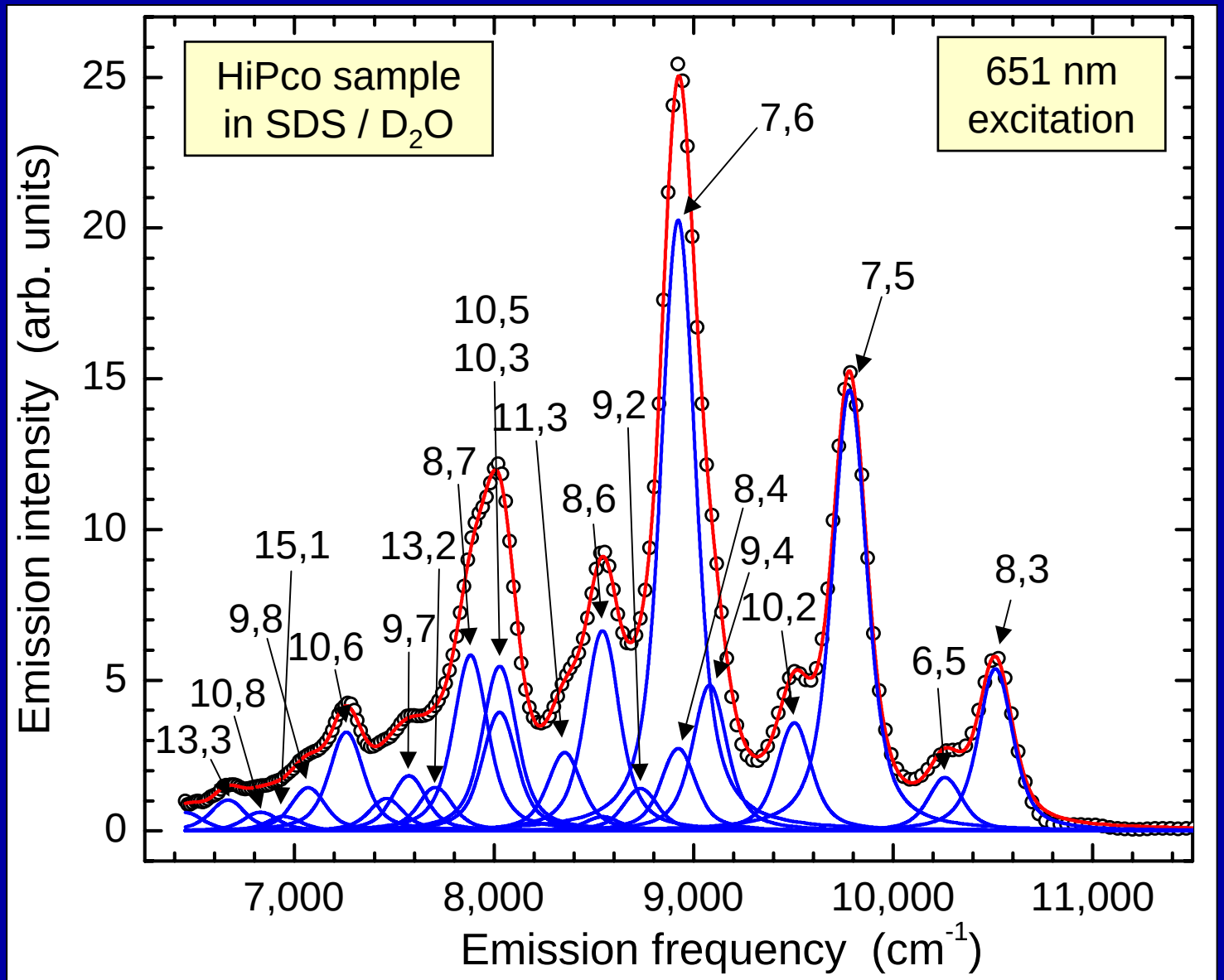
Analysis of Emission Spectrum to find Sample Composition



Fluorimetric Analysis of SWNTs

Advantages

- High sensitivity; small sample size (10 μg SWNT)
- Simple sample preparation (10 min sonication)
- Rapid, nondestructive measurements (few seconds)
- Secure (*n,m*) identification for tube diameter < 1.4 nm
- High selectivity against impurities, bundles, damaged nanotubes
- Simpler instrumentation than Raman
- Available as an automated commercial instrument

Disadvantages

1. Does not detect metallic SWNT
2. Does not detect bundled, damaged, or heavily derivatized SWNT
3. Not yet calibrated for quantitative analysis (but should be in future)

Conclusions

- Purification
  - Catalyst deactivation yields high purities with minimal carbon loss and sidewall damage
  - Cartridge system standardizes purification and is easily scaleable
- Length measurements
  - Alkylation in Li/NH_3 yields high propensity of individual nanotubes
  - Image analysis software (such as SIMAGIS) can be utilized to measure 1000+ nanotubes quickly with minimal user intervention
- Chirality/diameter determination
  - Fluorescence of semi-conducting tubes yields simple approach to identifying chirality
  - NanoSpectralyzer is a simple instrument capable of obtaining chirality distribution in less than 1 min

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