Evaluation of the Quality of SWNT Prepared by the CoMoCAT Catalytic Method

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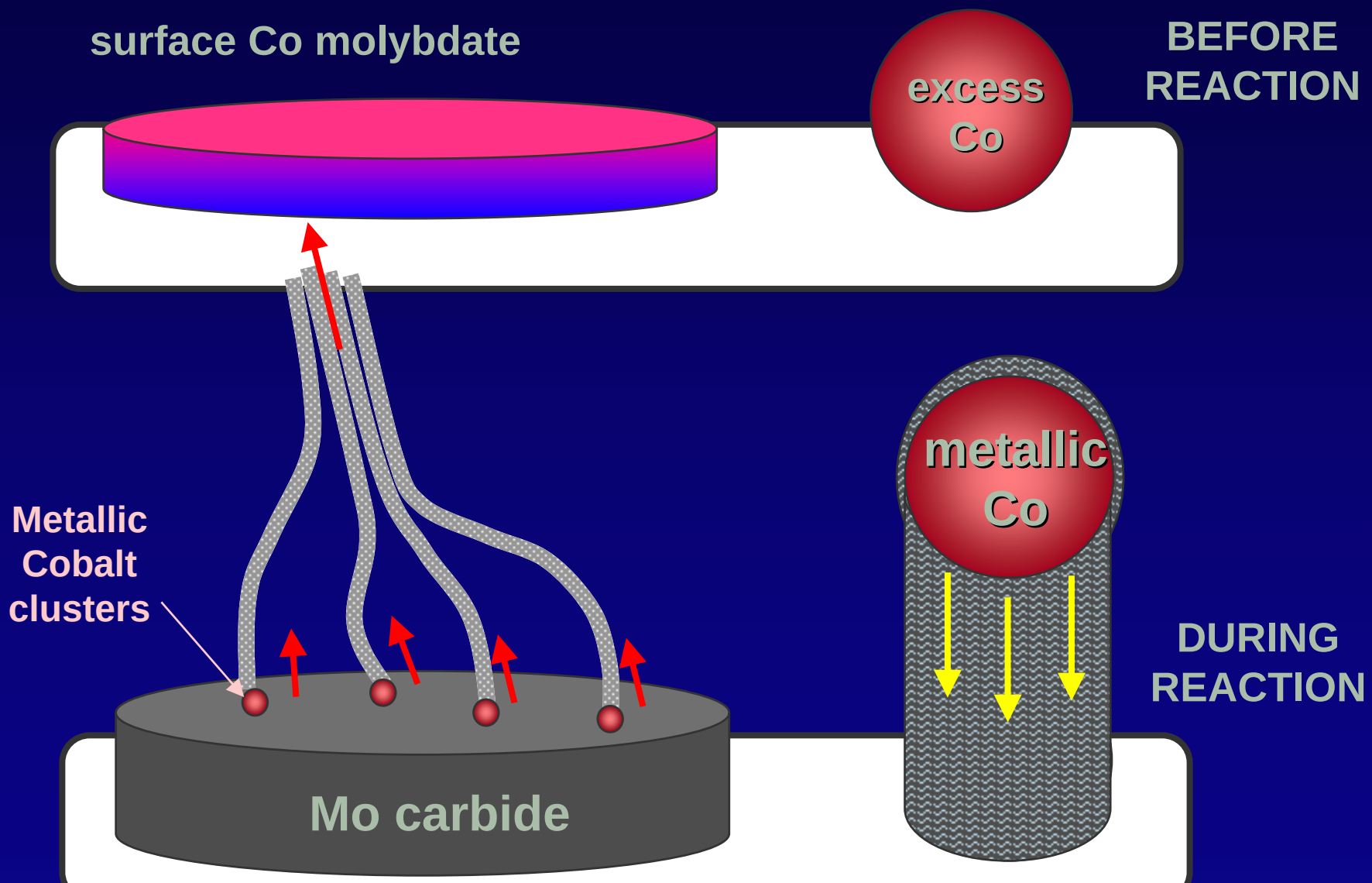
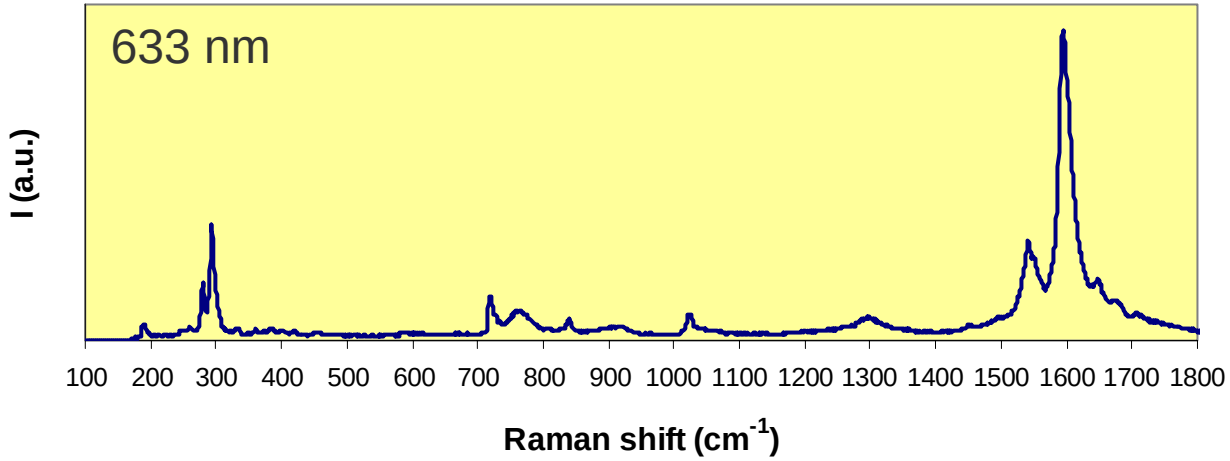
University of Oklahoma and SouthWest Nanotechnologies (SWeNT)

CoMoCAT Growth Mechanism

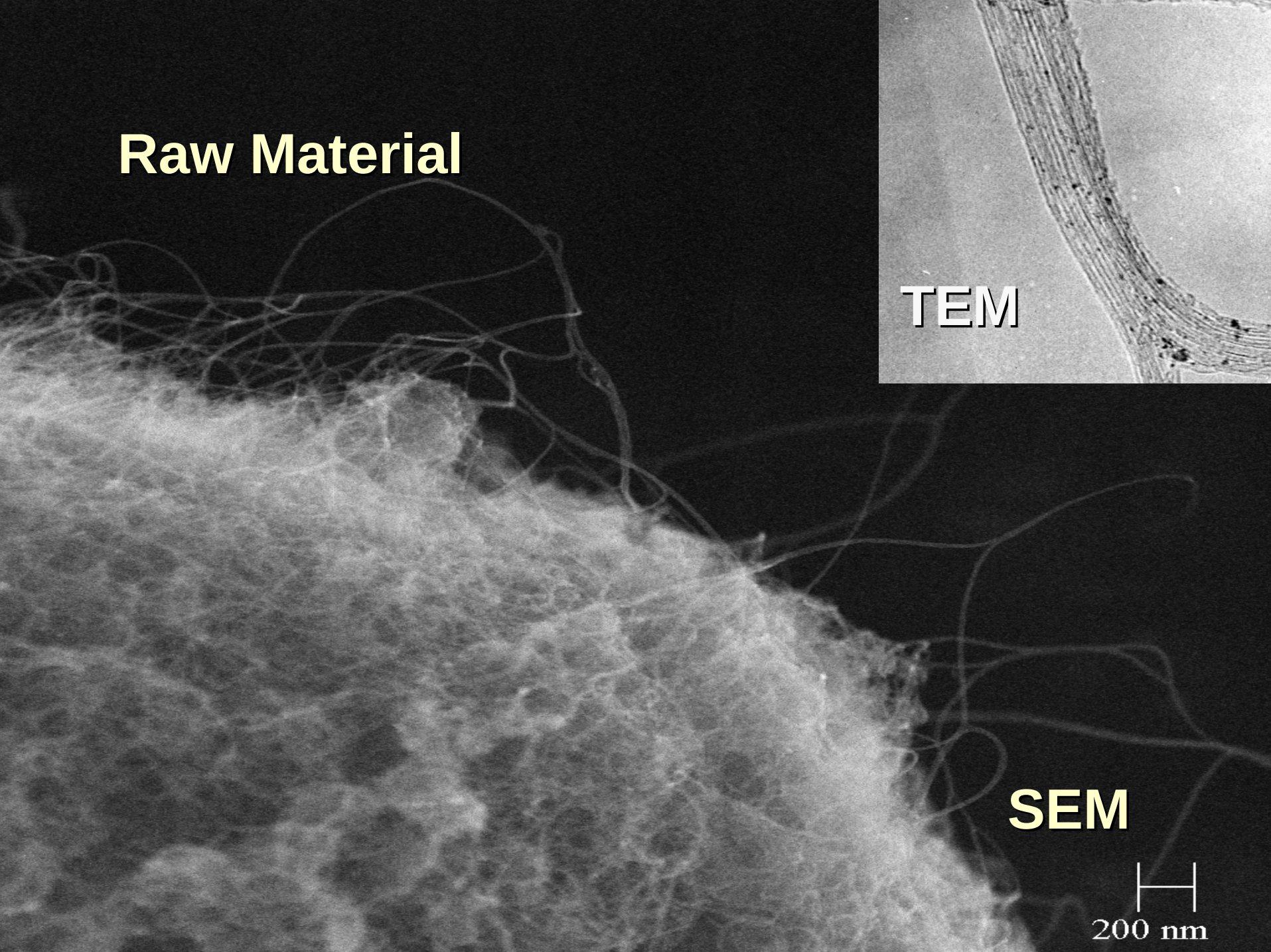


CoMoCAT™ Process

- Supported catalyst $Co:Mo/SiO_2$
- T = 750-950 °C
- P = 1-7 atm
- $2CO \rightarrow C + CO_2$



Raw Material



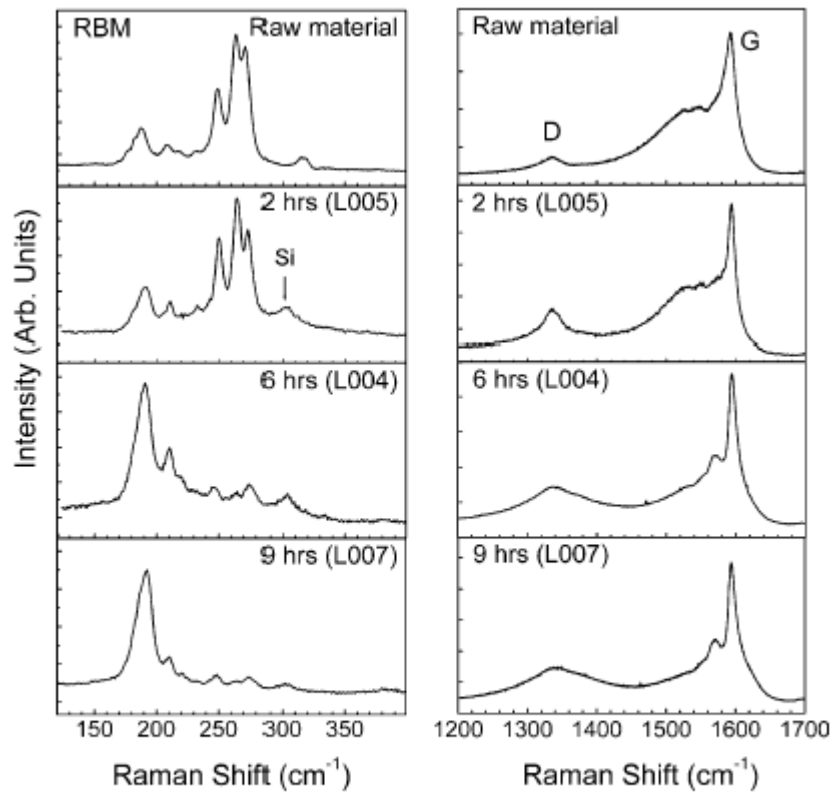
(Mild) Purification of CoMoCAT nanotubes

Purification of SWNT made from other methods:

- No catalyst support
- Large (C encapsulated) metal particles
- Larger Average SWNT diameter and bundle size

CoMoCAT can be purified with diluted HF after dry pre-oxidation

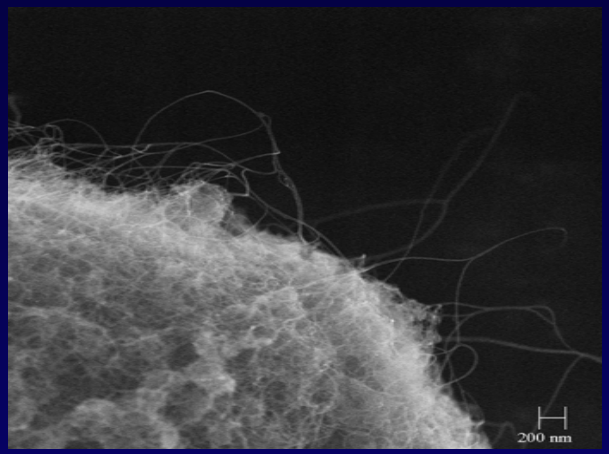
Small diameter nanotubes are more susceptible to acid attack



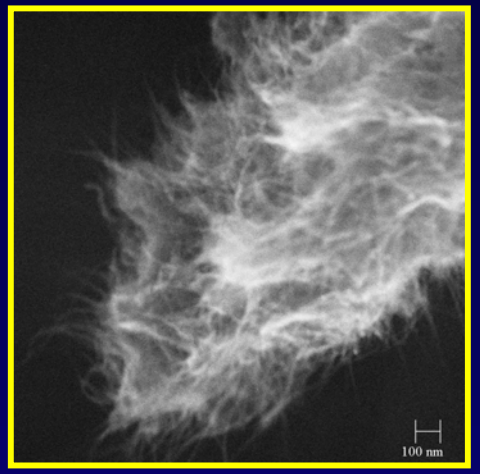
Effect of sonication time in H_2SO_4:HNO_3 (3:1) solution on HiPCO nanotubes. Excitation laser: 514 nm.

Wiltshire, et al. Chemical Physics Letters (2004), 386(4-6), 239-243

Purification and Suspension of CoMoCAT Nanotube



SWNT gel
Patent Pending



Freeze-dried
pure material

Dry
Oxidation
at 250 C

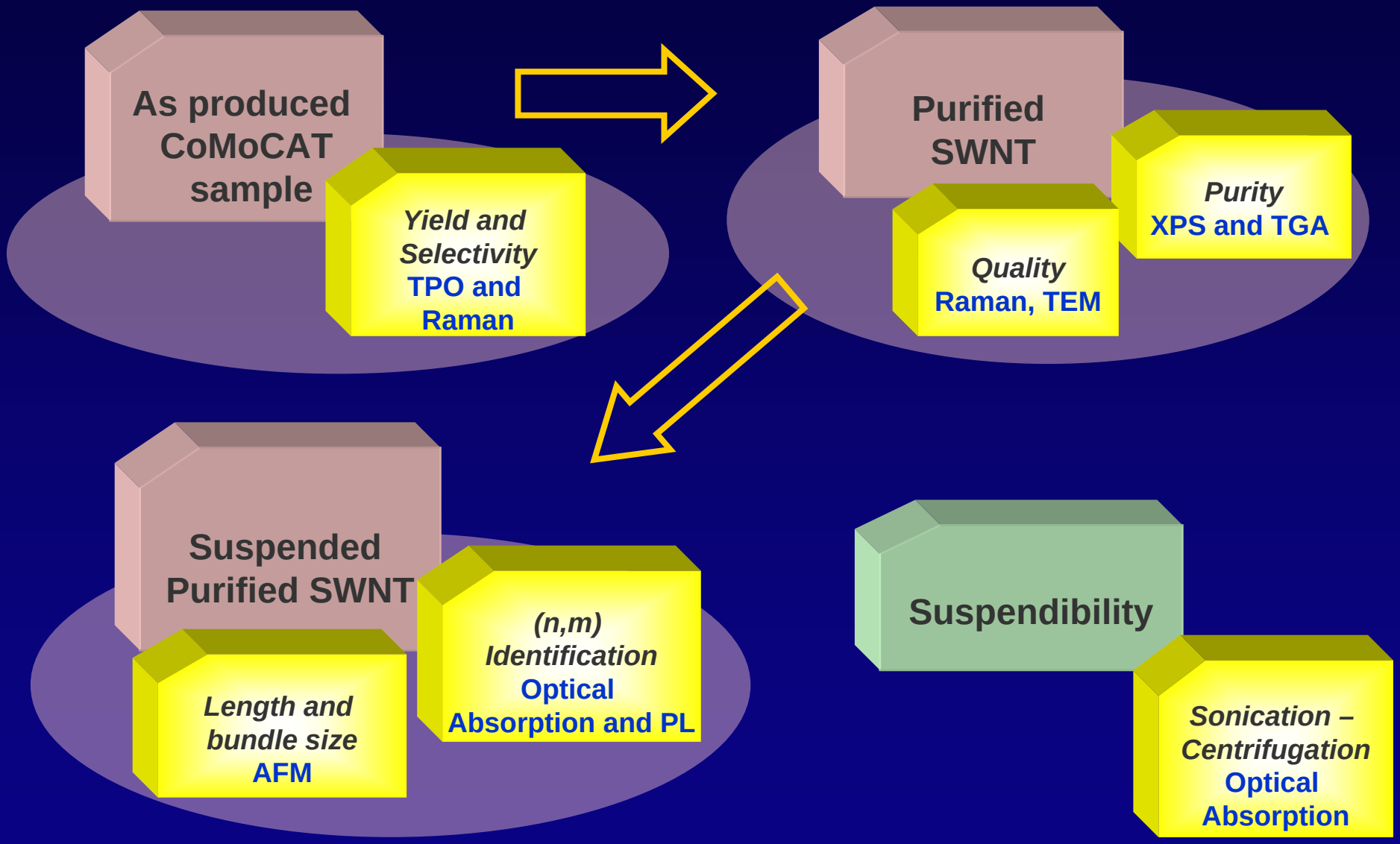
HF to remove silica support

Stable
suspension in
Surfactant
solution

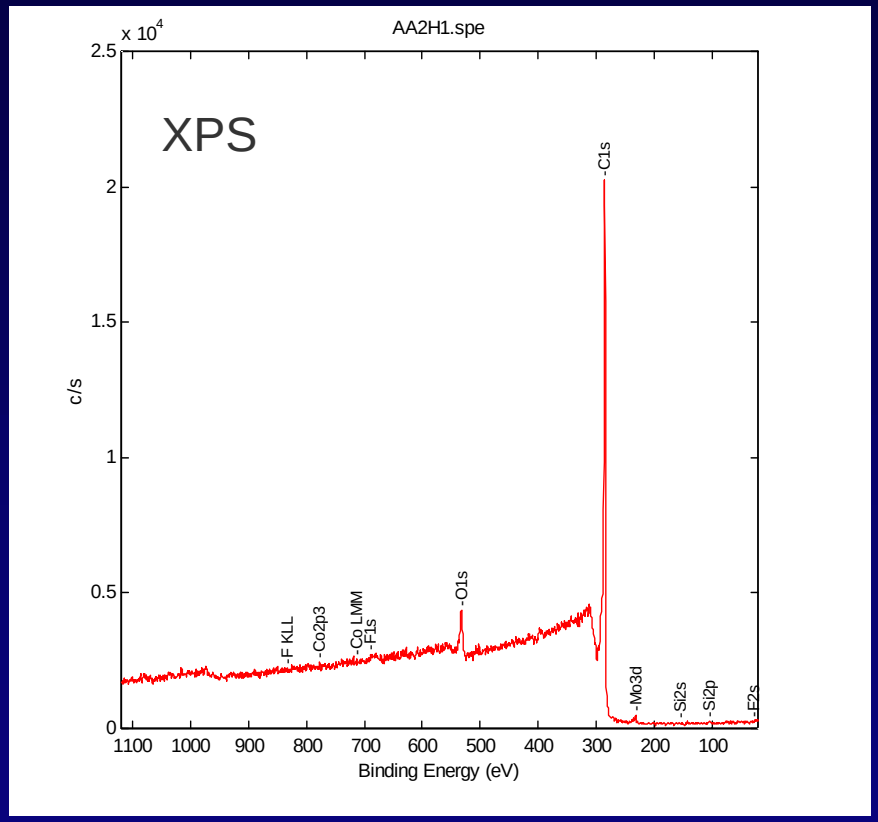
Quality Assessment Protocol

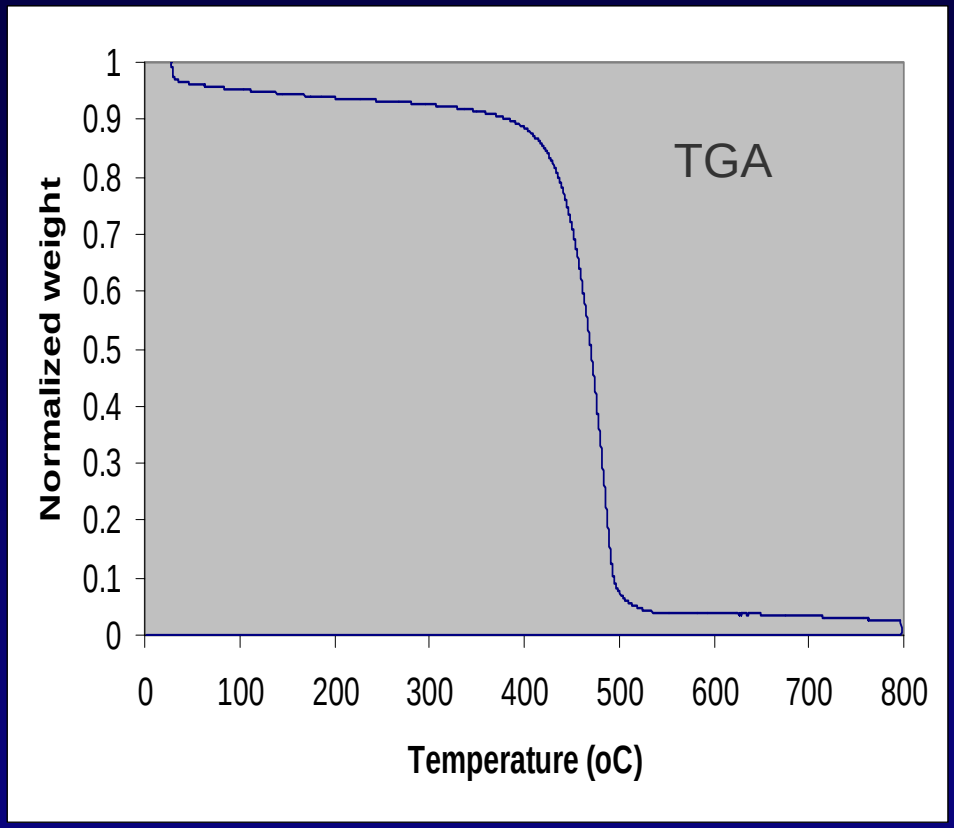
- X-ray Photoelectron Spectroscopy (XPS)
- Thermogravimetry Analysis (TGA)
- Temperature Programmed Oxidation (TPO)
- Electron Microscopy (SEM, TEM)
- Raman Spectroscopy
- Photoluminescence
- Optical Absorption (NIR-UV-Vis)
- AFM / STM

Quality Assessment Protocol



XPS and TGA used to Determine Impurity Levels

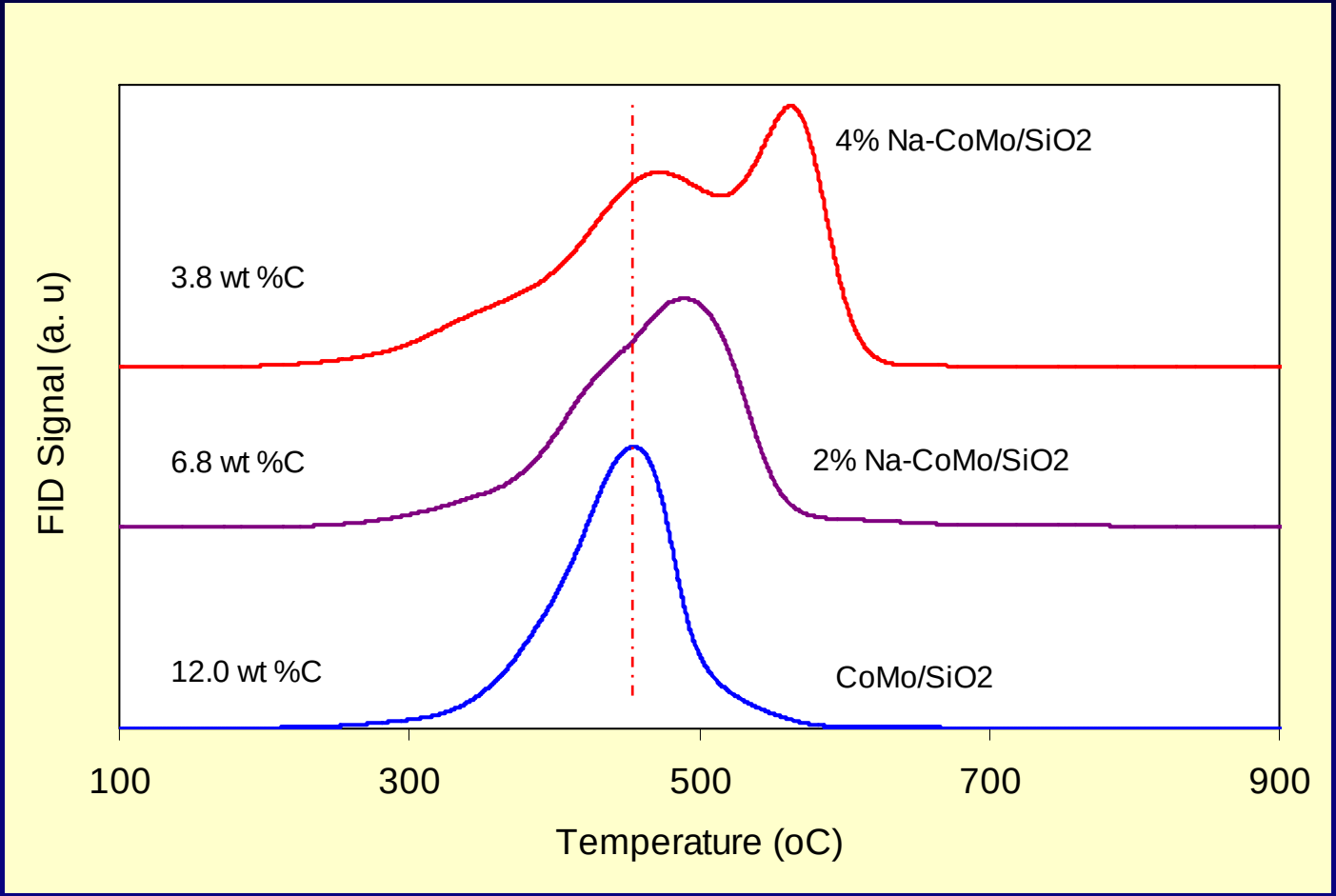




Chemical composition by XPS analysis (A%)					
C	O	F	Si	Co	Mo
96%	3.79%	0.11%	0.00%	0.02%	0.17%

Purified CoMoCAT nanotubes contain less than 3 wt % metal impurities

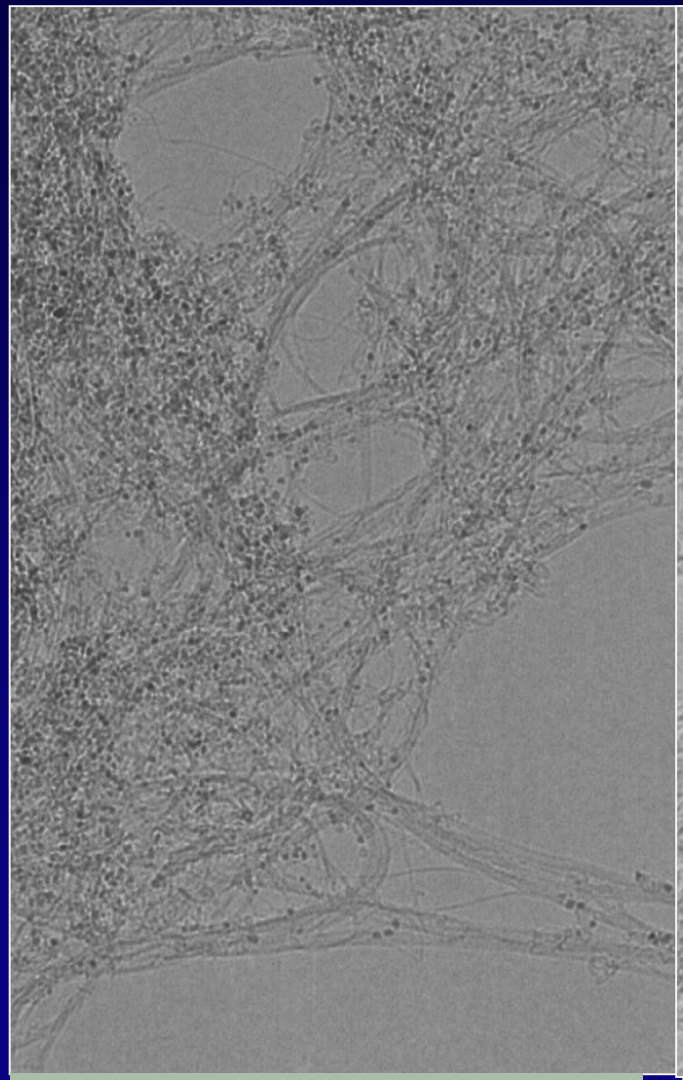
TPO quantitative for C yield and semi-quantitative for SWNT selectivity



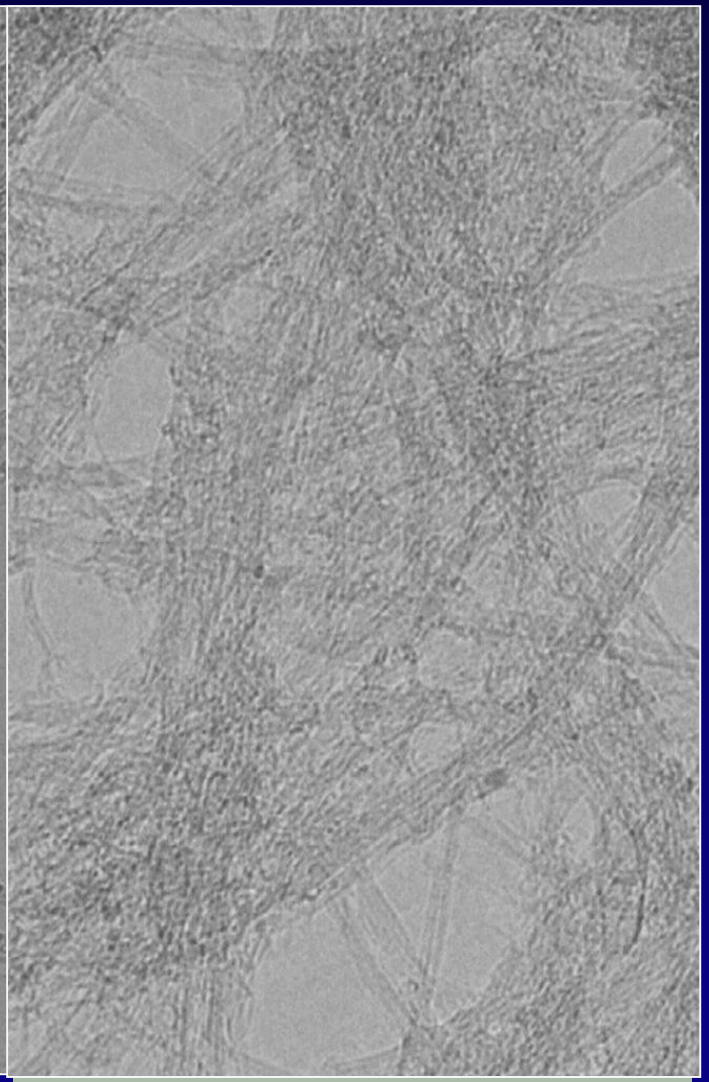
CoMoCAT catalyst exhibits higher yield and SWNT selectivity than Na-containing catalysts

633 nm

Electron Microscopy (TEM)



No oxidation

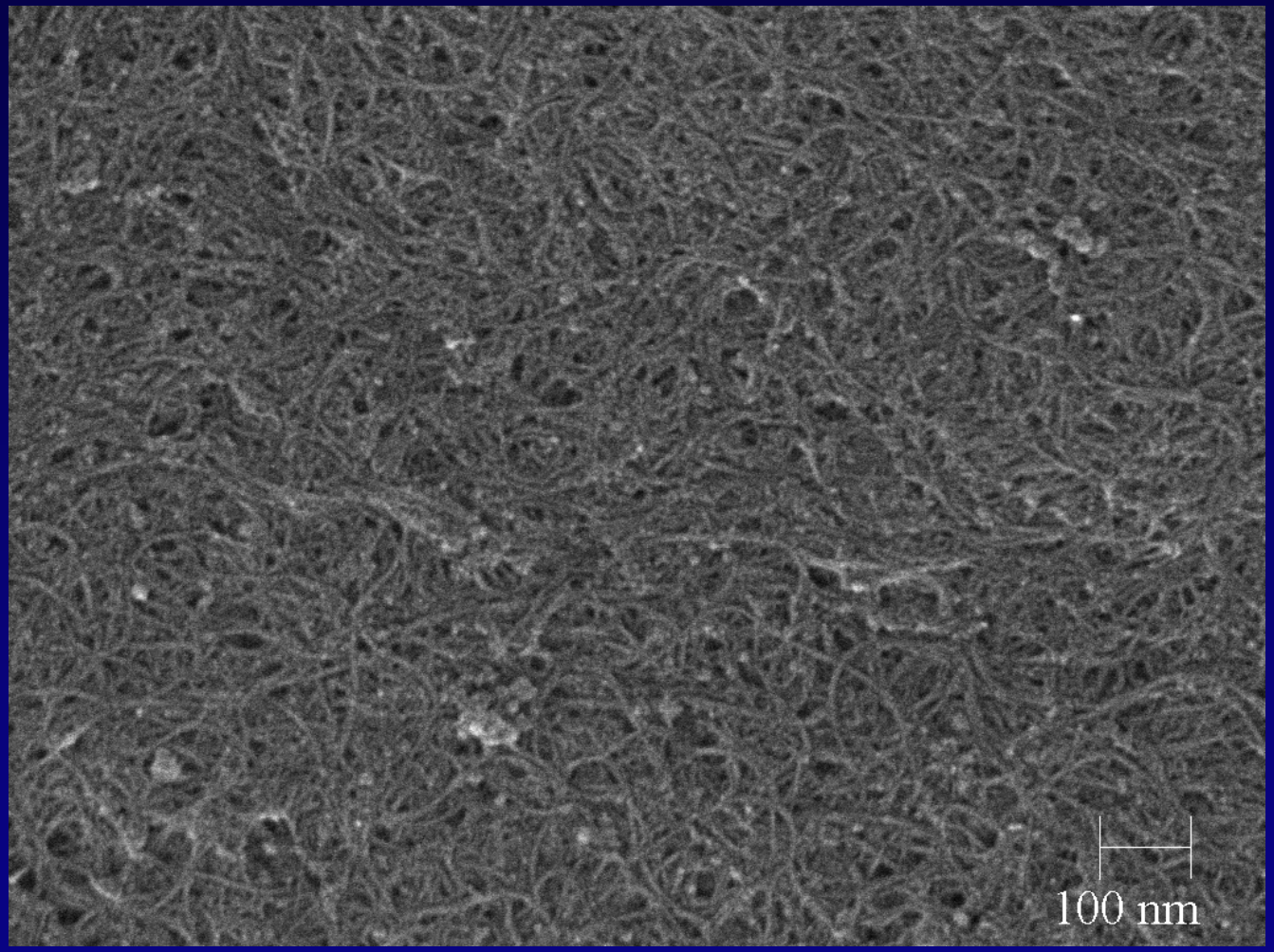


Oxidation in air @250°C

Observations:
a) SWNT Vs. other forms of carbon
b) Residual catalyst particles

Example: Here, TEM shows a significant difference in nanotube purity as a result of the oxidation treatment, prior to the acid attack

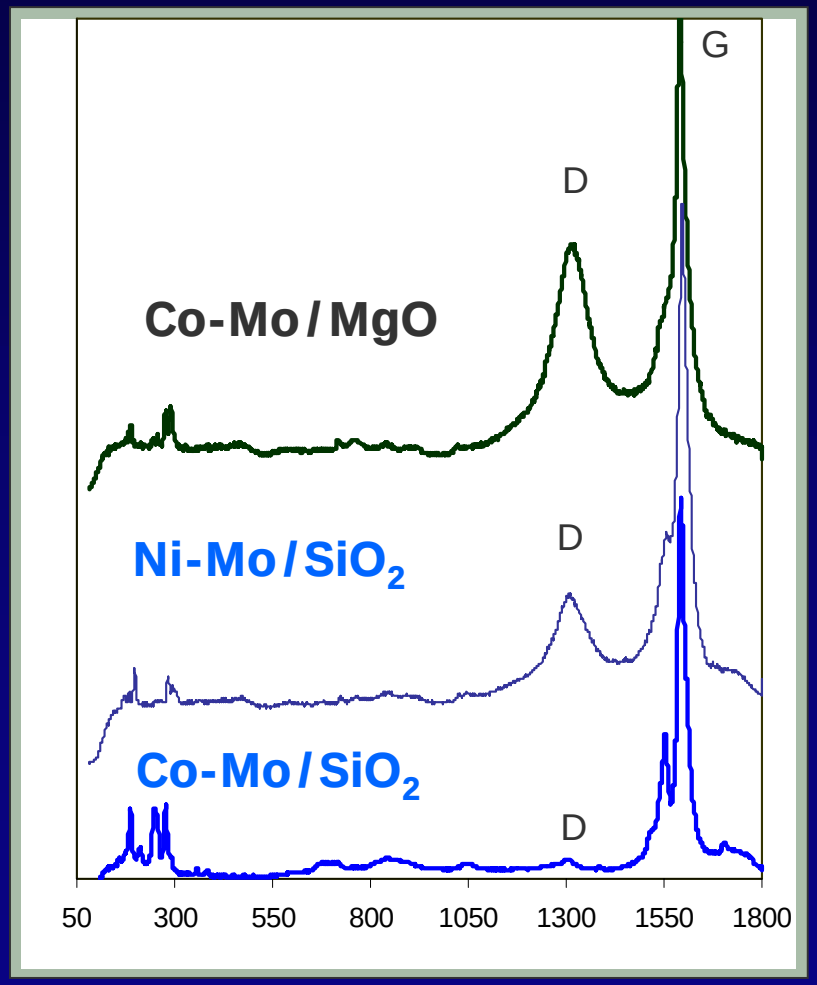
Electron Microscopy (SEM)



Purified CoMoCAT nanotubes

Raman Spectroscopy

Raman spectra of SWNT from different catalysts



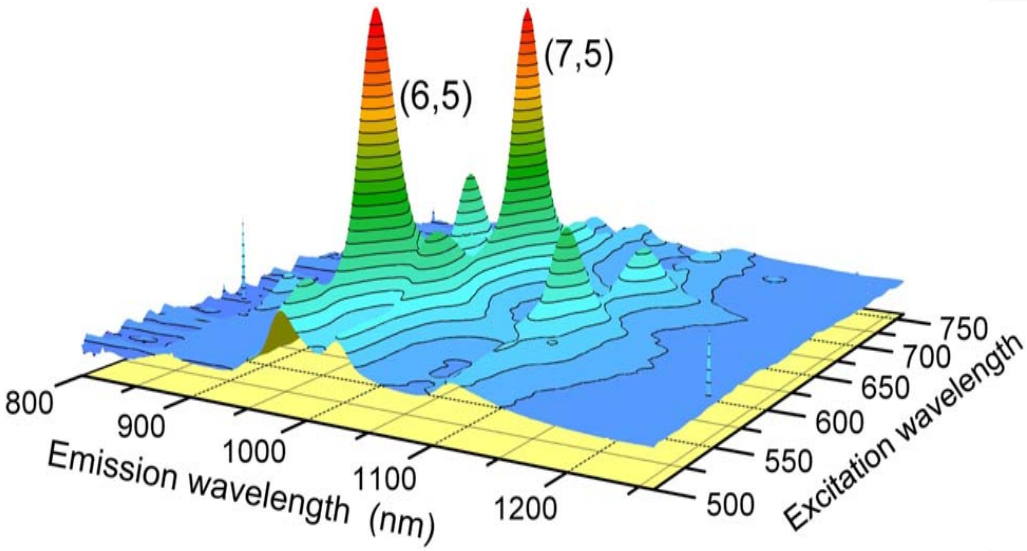
Quality Parameter = 100 x (G/D+G)

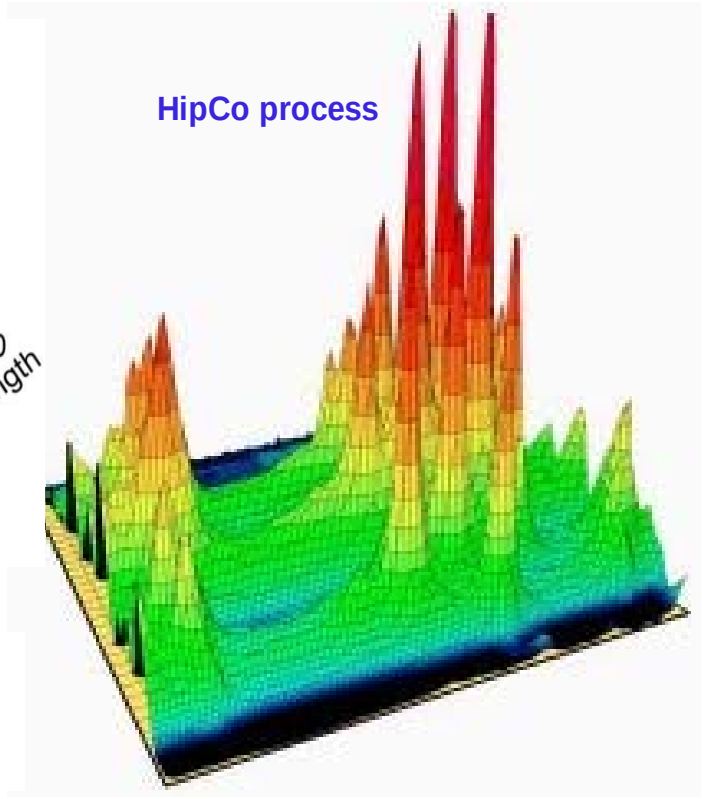
Catalyst		Quality Parameter
Fe		47
FeMo 2:1		66
FeMo 1:1		66
FeMo 1:2		65
Co		63
CoMo 2:1		89
CoMo 1:1		92
CoMo 1:2		**95**
Ni		76
NiMo 2:1		77
NiMo 1:1		64
NiMo 1:2		56
Mo		62

NOTE: RBM not a reliable way of determining all SWNT structures present in sample

Photoluminescence - identifies (n,m) structures

Obtained at Rice University by Weisman et al. (2003)

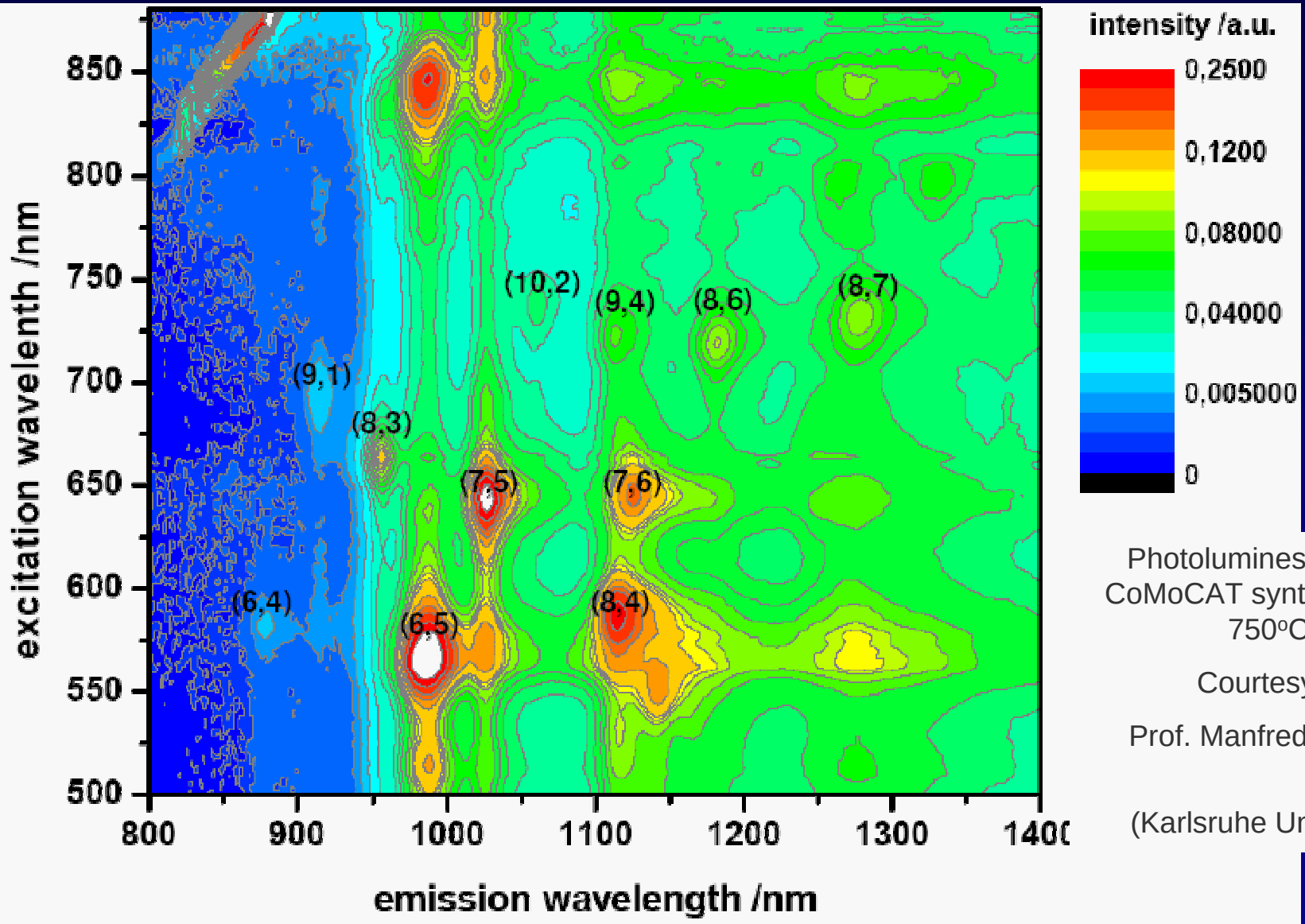




Spectrofluorimetric analysis of CoMoCAT (Left) and HiPCO™ (Right) samples. The comparison reflects the much narrower distribution of diameter and chirality

LIMITATION of this TECHNIQUE: It only probes semiconducting nanotubes

Photoluminescence



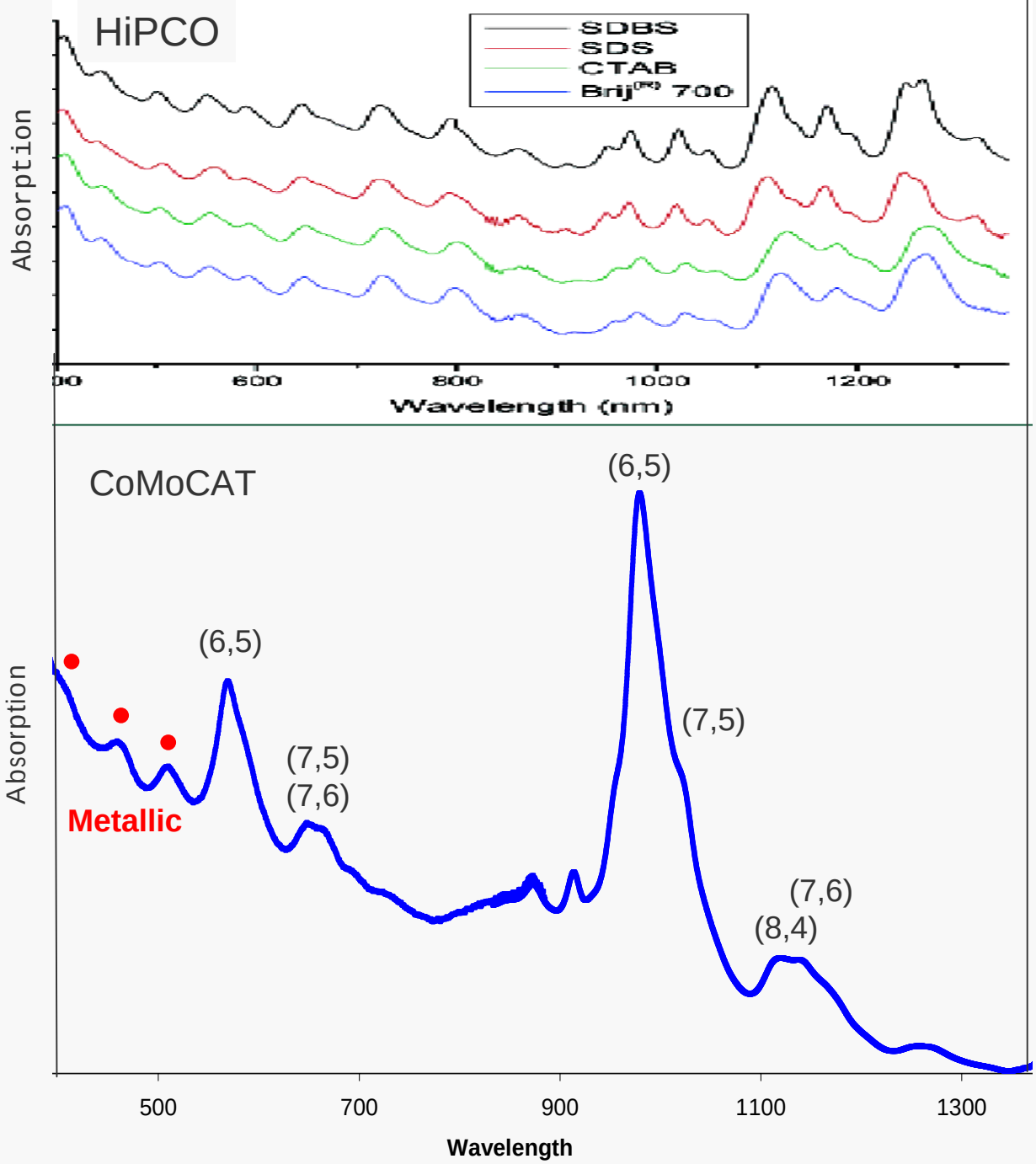
Photoluminescense of CoMoCAT synthesized at 750°C.

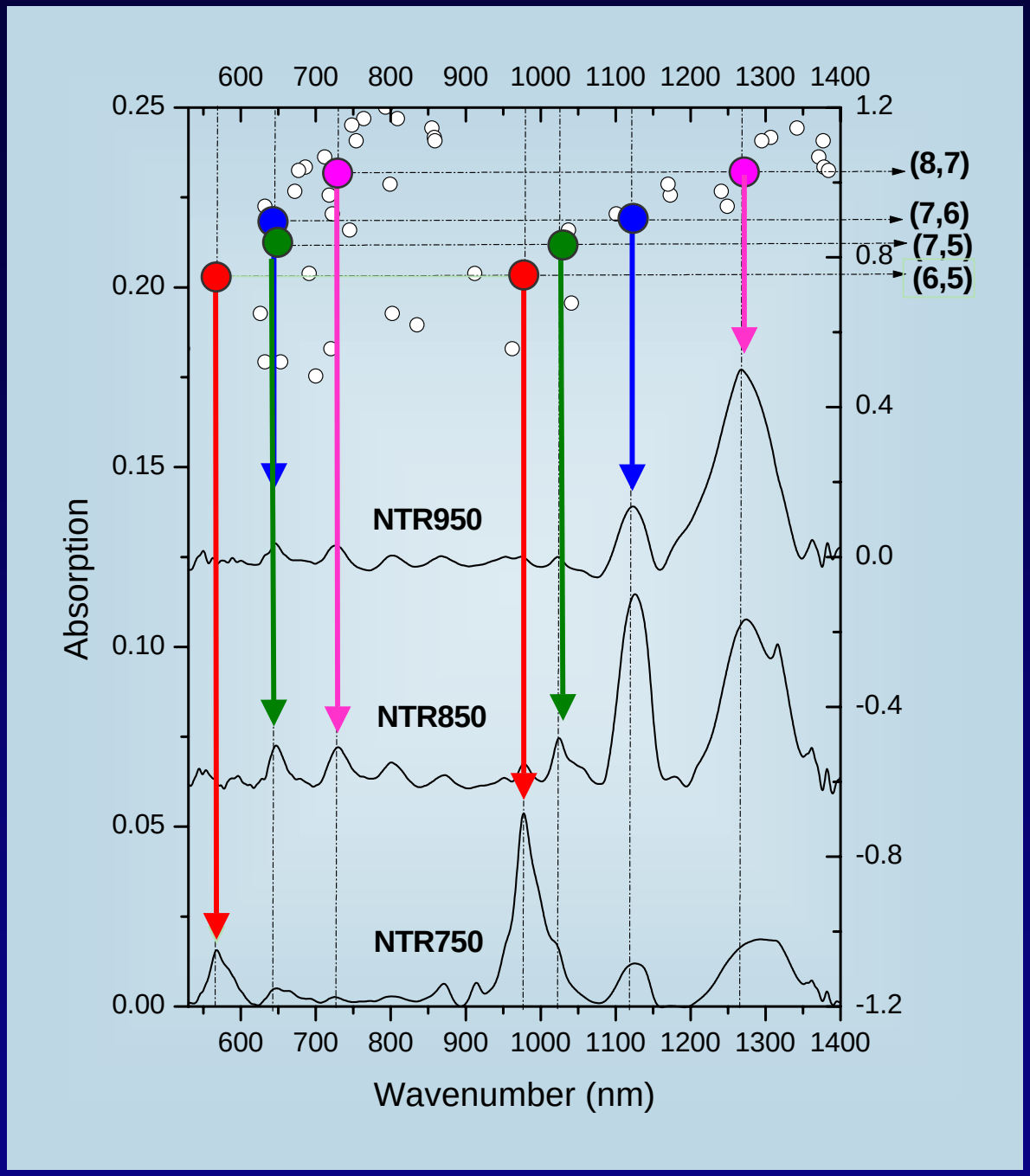
Courtesy of

Prof. Manfred Kappes

(Karlsruhe University)

Structure-Assigned Optical Absorption Spectra





Effect of Reaction Temperature on SWNT Diameter

Optical Absorption

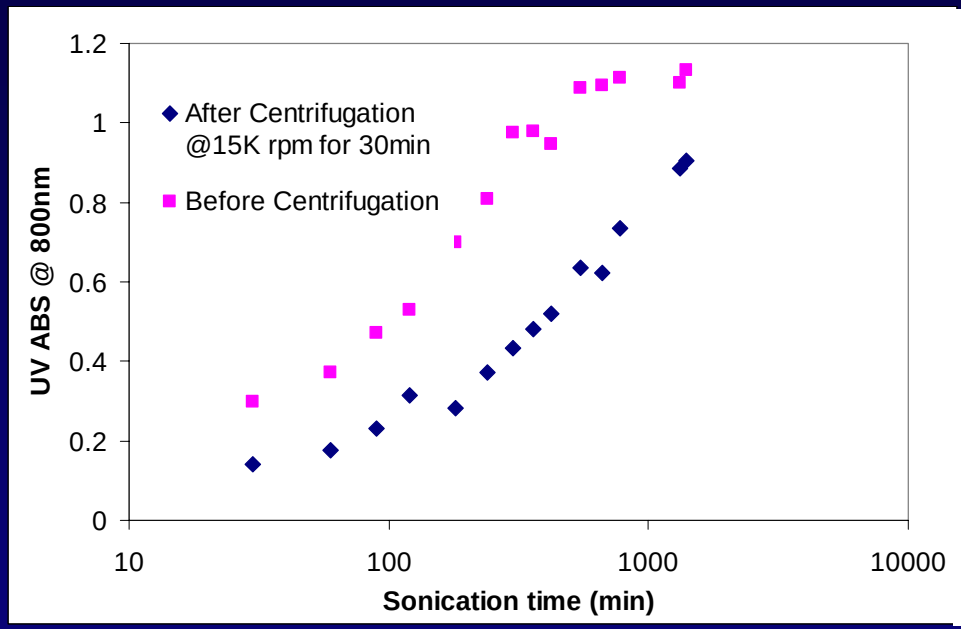
Uses of Optical Absorption in SWNT Characterization

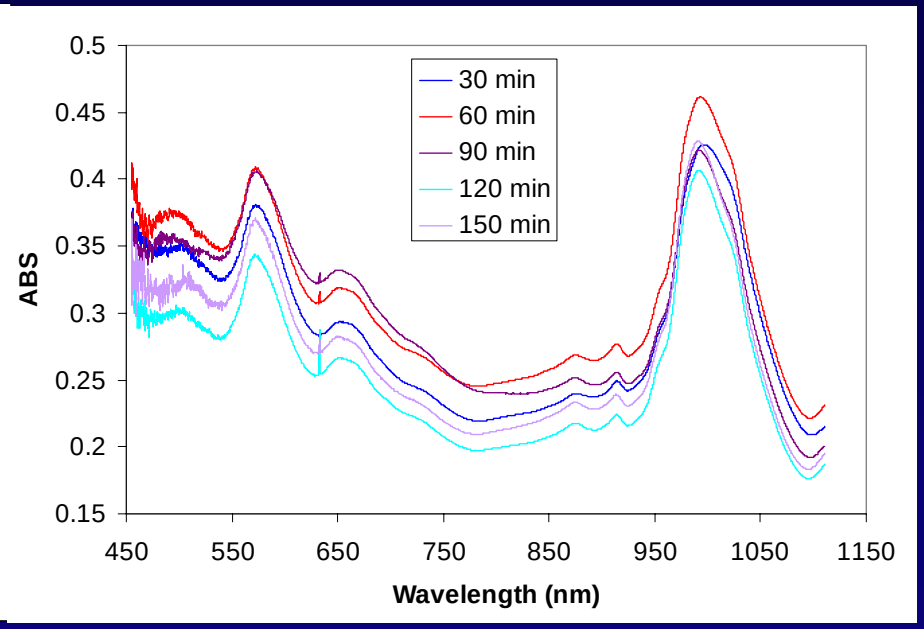
- (n,m) identification on different samples (varying catalyst and synthesis conditions)
- Assessment of SWNT dispersibility in different media (type of surfactant)
- Optimization of sonication and centrifugation conditions
- Functionalization and De-functionalization

Effect of sonication with NaDDBS on SWNT dispersion

Horn Sonicator: 20 KHz – 20 % amplitude - cooling in ice

10 mg SWNT / 100 ml



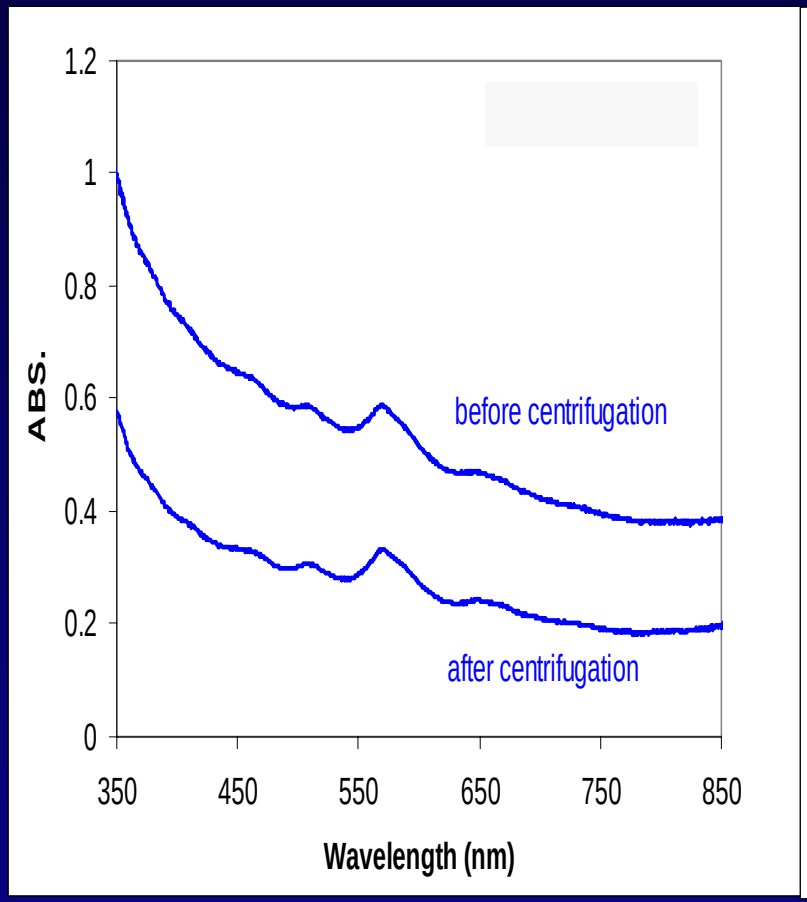


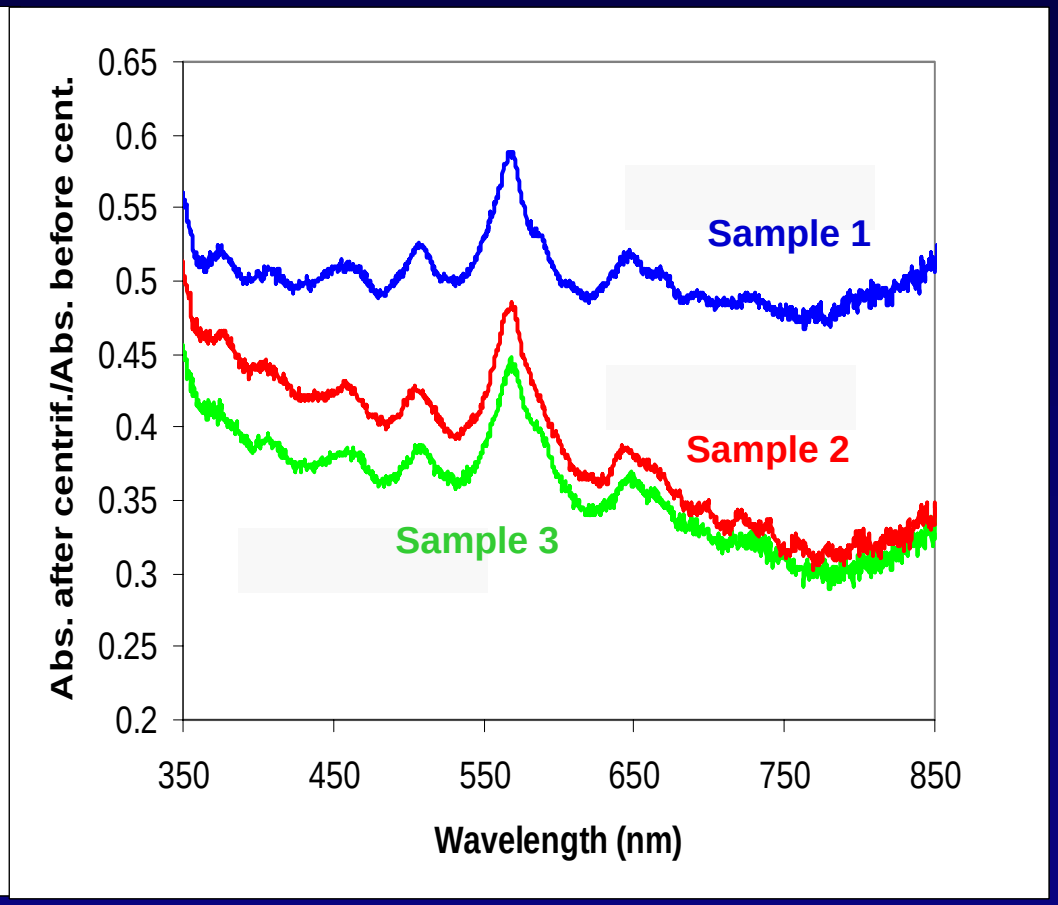
Recommendation:

Always specify:

- Sonication method (Horn Vs. Bath)
- Sonicator Power and Frequency
- Liquid of Volume
- pH of solution
- Cooling method
- SWNT concentration

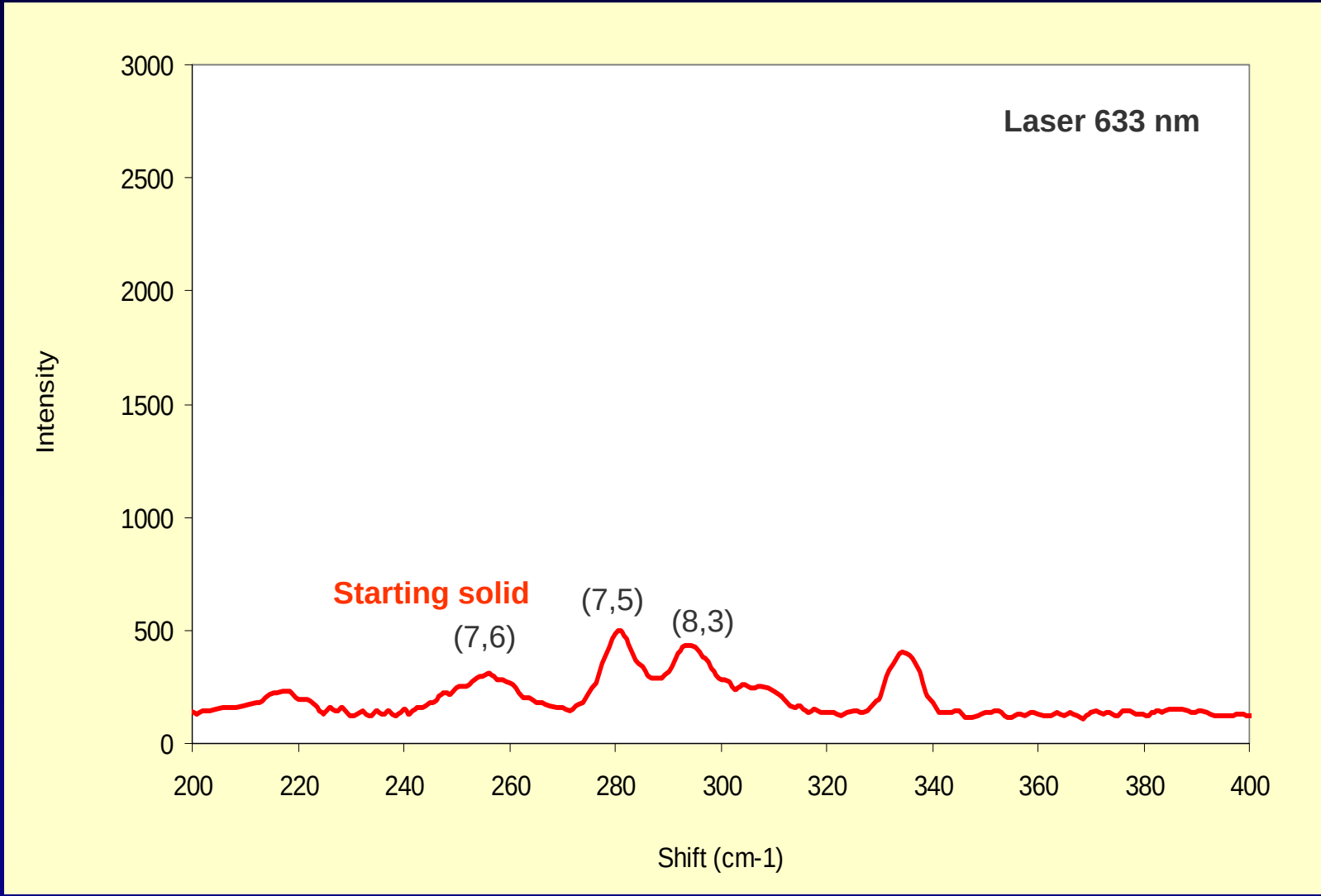
Absorption Ratio Between After/Before Sonication





This ratio is a good indication of the dispersibility of sample

Raman of Solid and Suspended Samples



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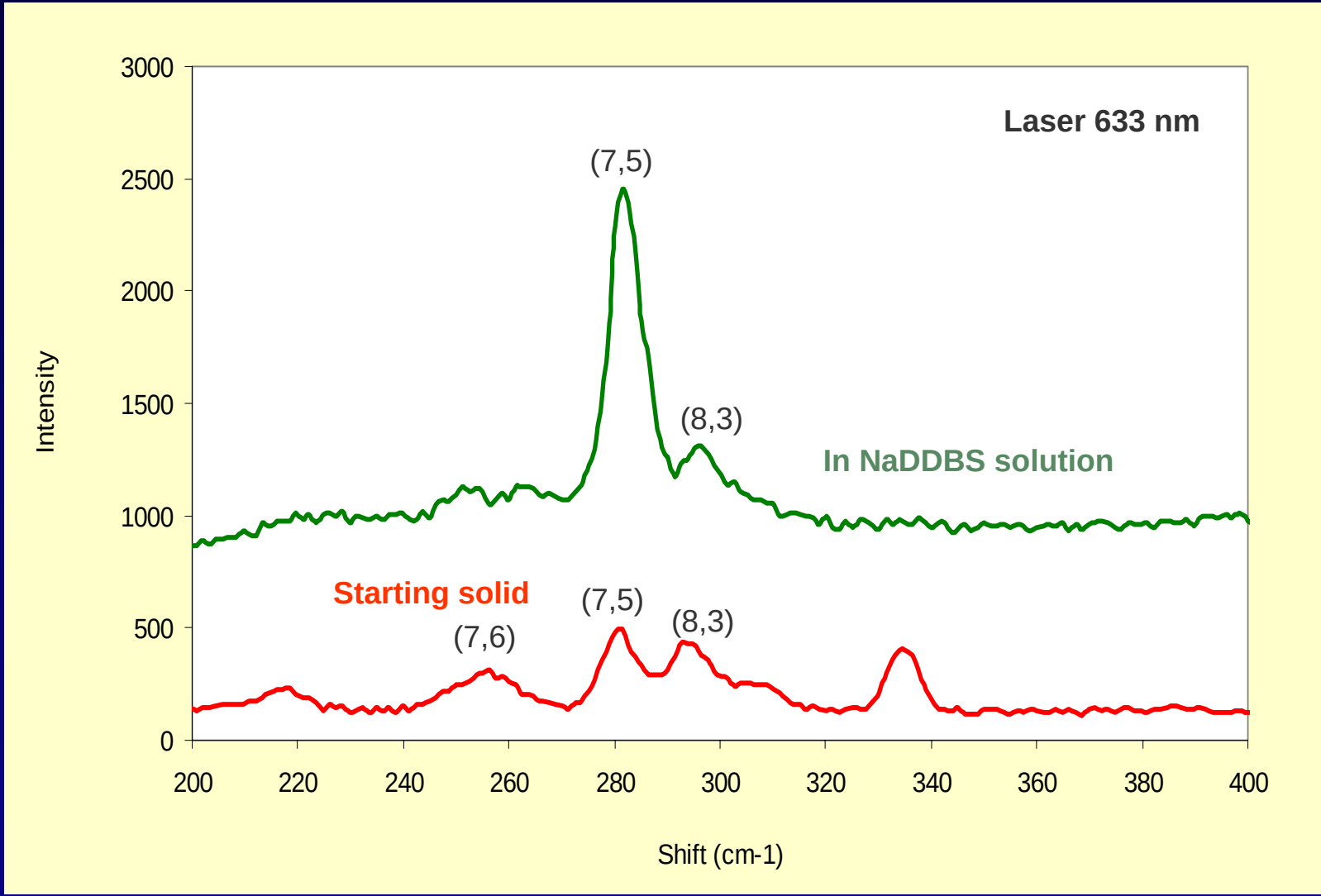
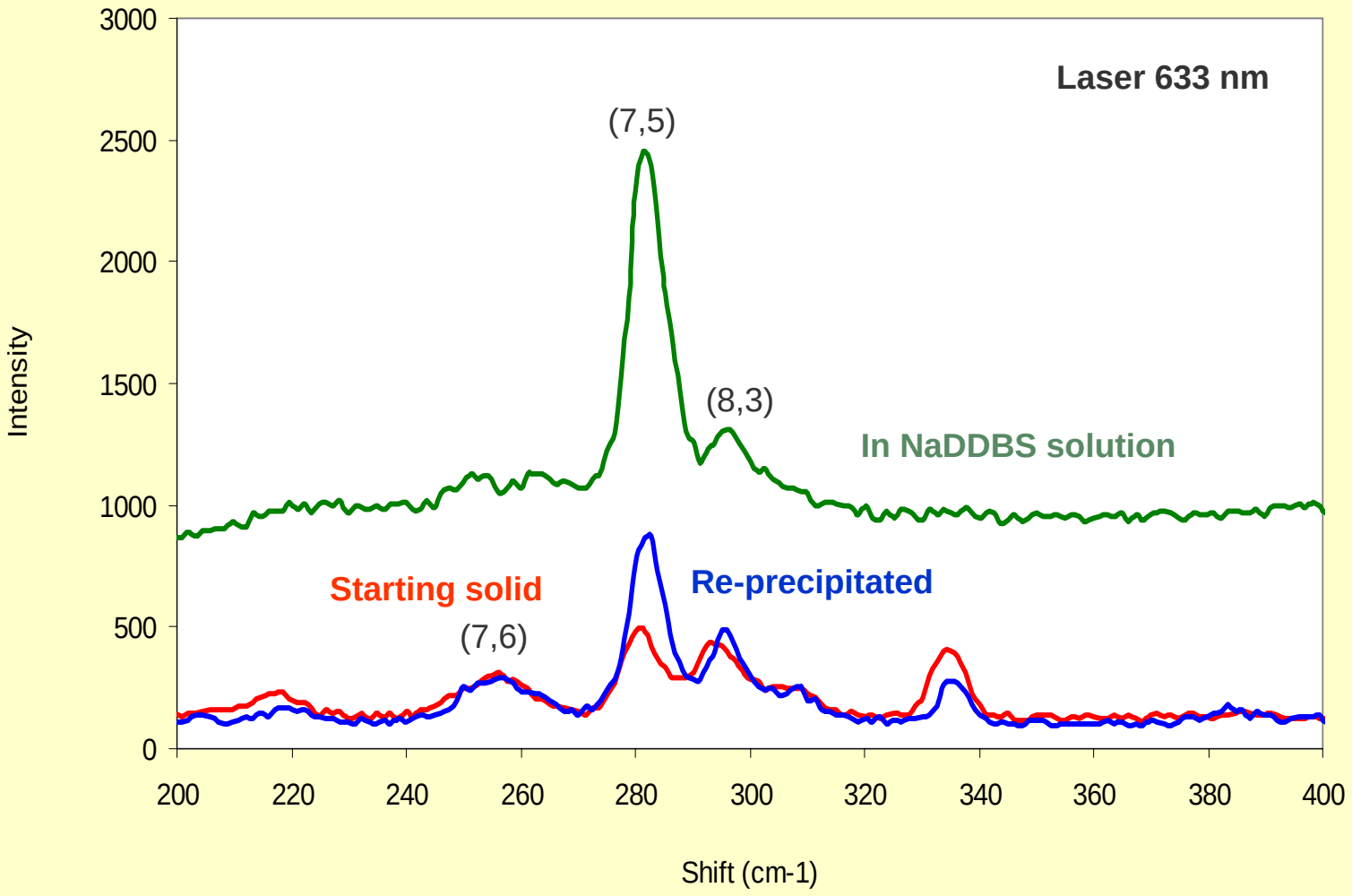
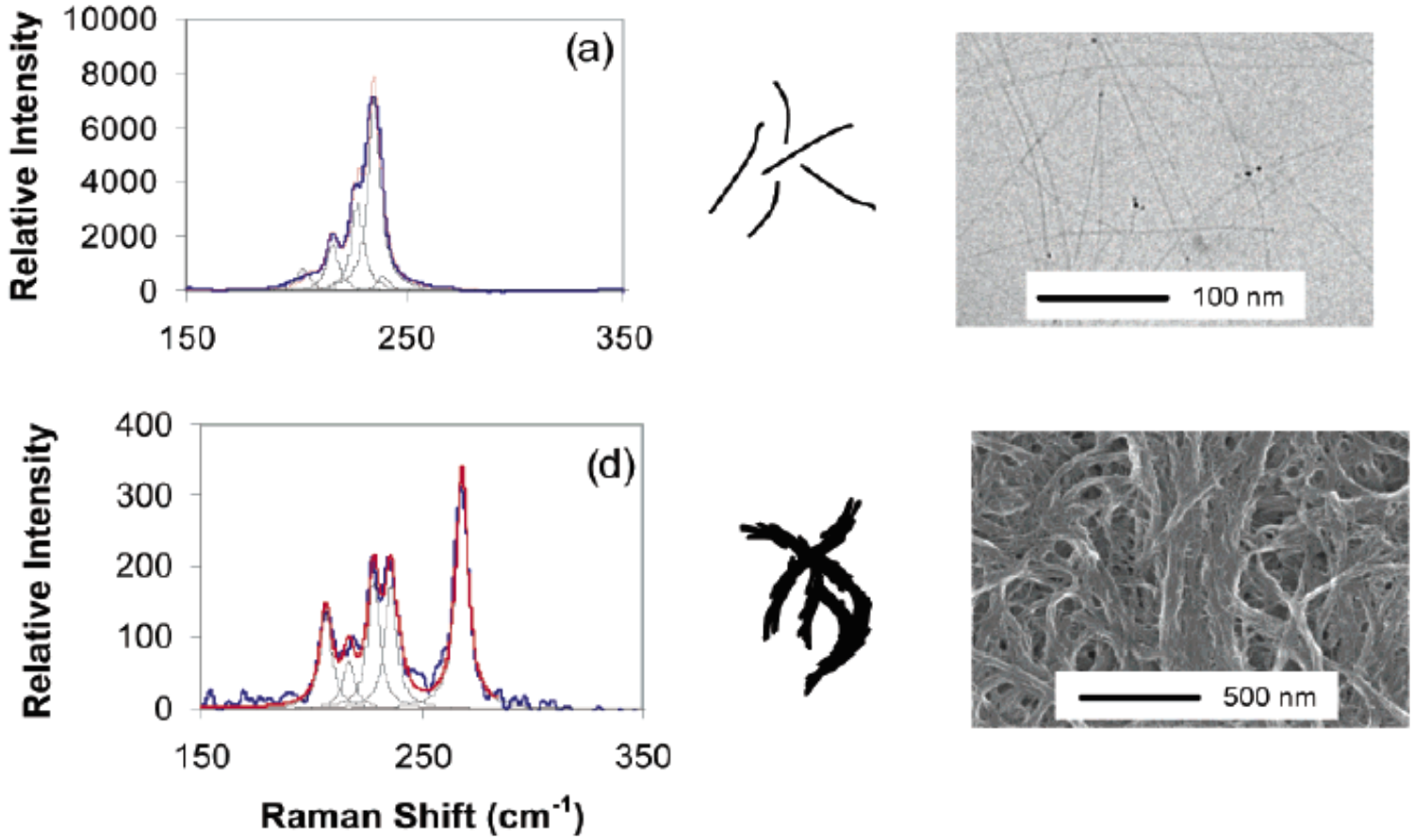


Raman of Solid and Suspended Samples



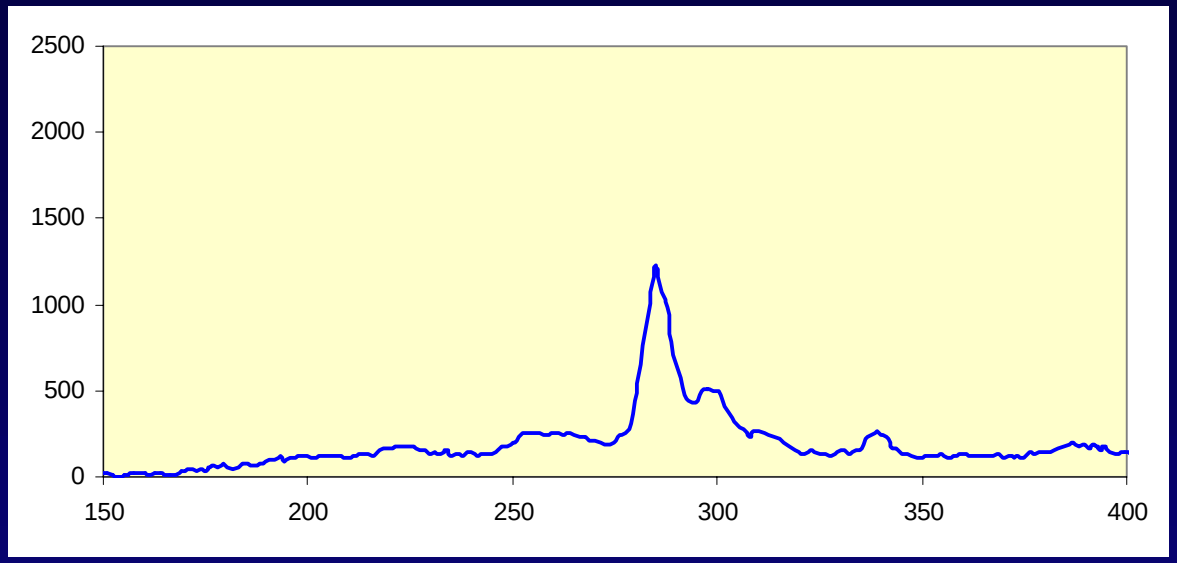
Modification of Raman Spectra by Bundling and Thermal Effects



Daniel A. Heller,† Paul W. Barone,‡ John P. Swanson,‡ Rebecca M. Mayrhofer,‡ and Michael S. Strano*,‡

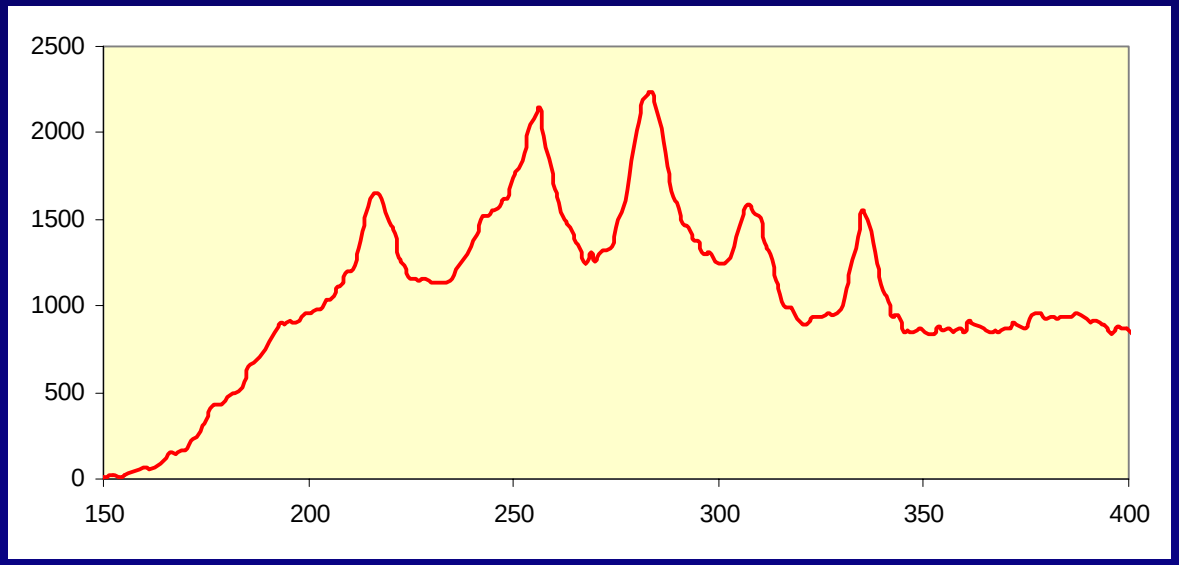
J. Phys. Chem. B **2004**, *108*, 6905−6909

Modification of Raman Spectra by Bundling and Thermal Effects



Power = 0.1 mW

Raman spectrum taken with 1 mW power with filter that cuts 90 % of power



Power = 1 mW

Raman spectrum taken with 1 mW power after removing the filter

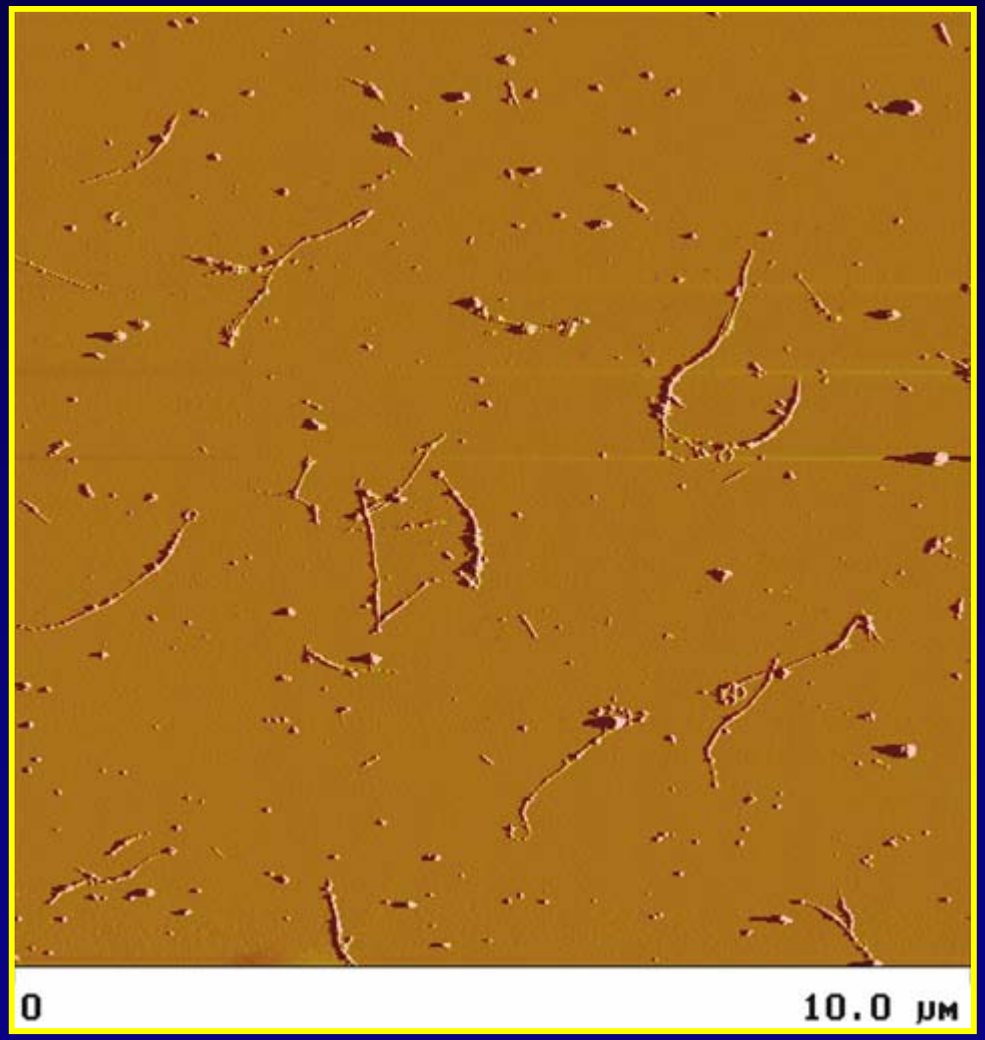
Atomic Force Microscopy (AFM)

AFM image of
nanotube produced by the
CoMoCAT process at 750 C

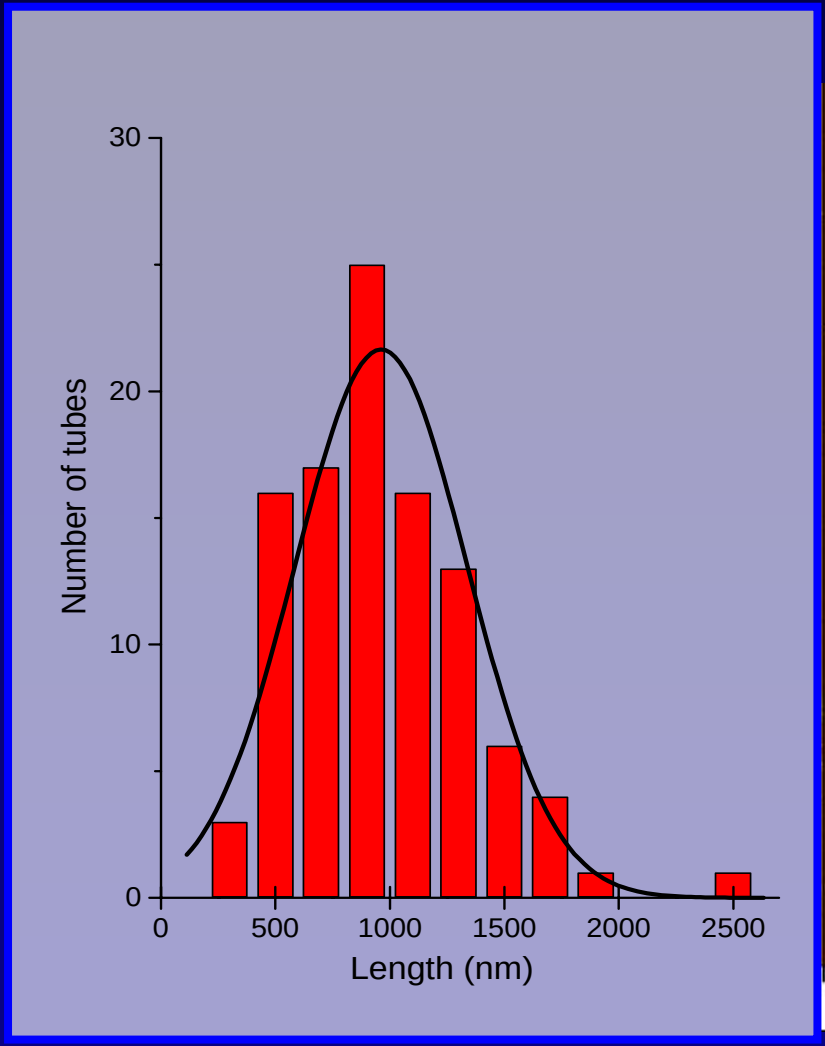
Suspended in DMF;
Spin coated to deposit on a
Si wafer

Source of Impurities?

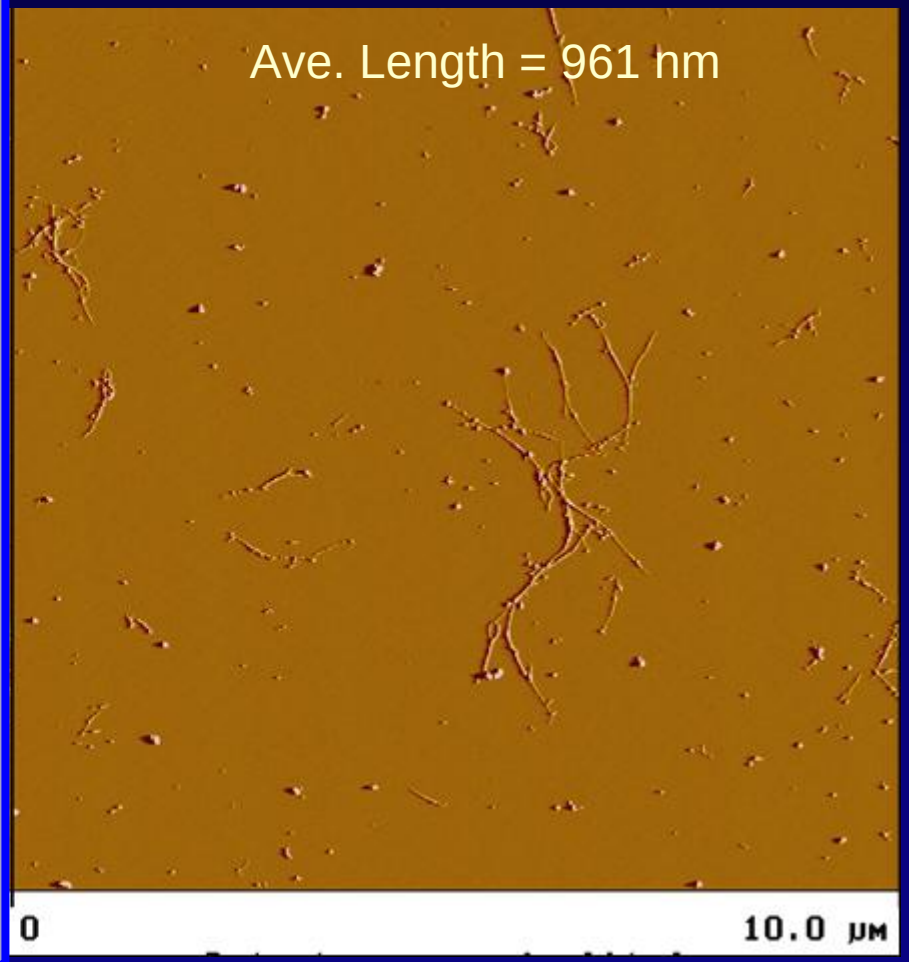
a) Sample (catalyst – amorphous C)
b) Solvents used



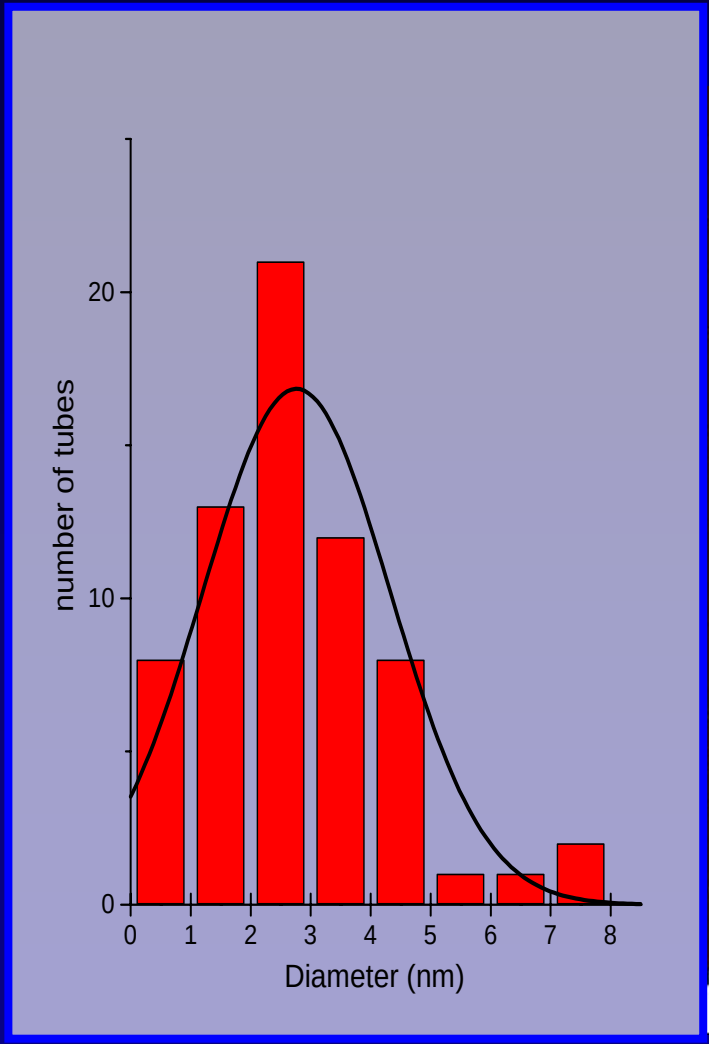
Length Distribution of Purified CoMoCAT Nanotubes



Purification:
Stir 5 min in 10% HF



Bundle Size Distribution of Purified CoMoCAT Nanotubes



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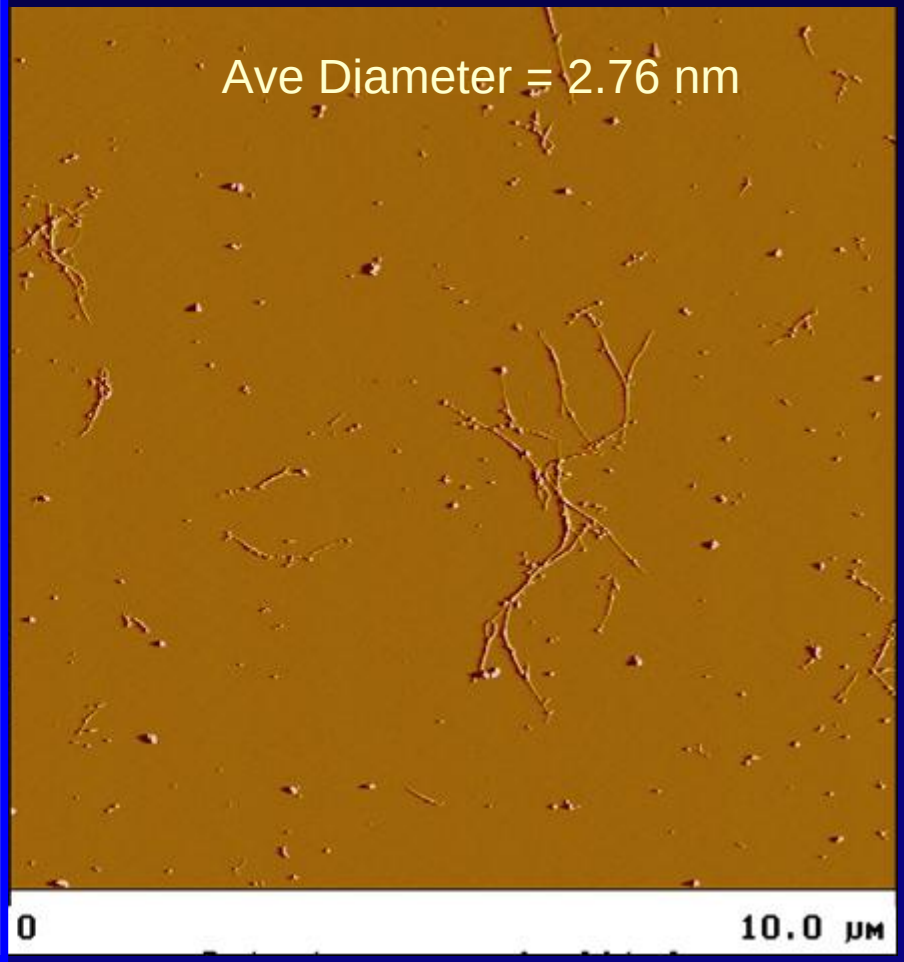
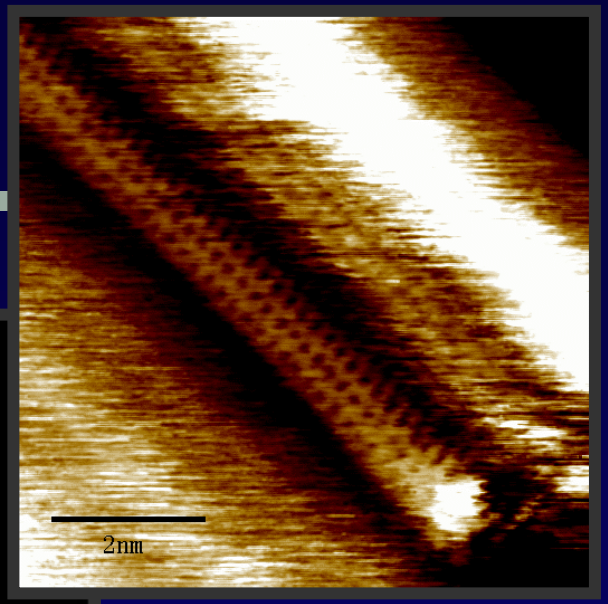
Stir 5 min in 10% HF

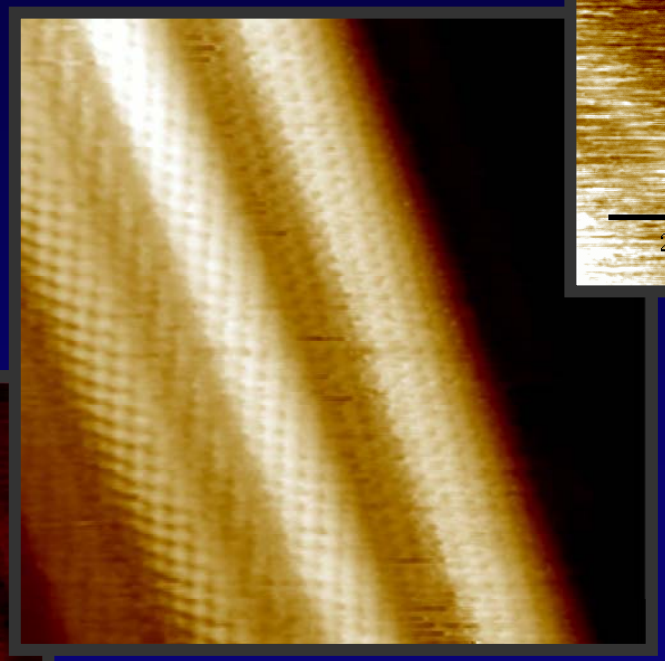


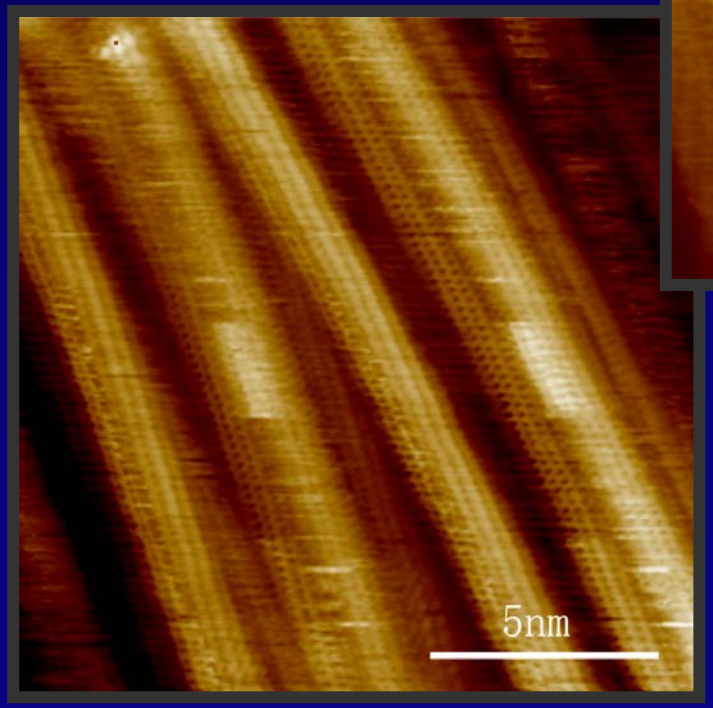
Scanning Tunneling Microscopy (STM)

STM image of nanotube produced by the CoMoCAT process at 750 C

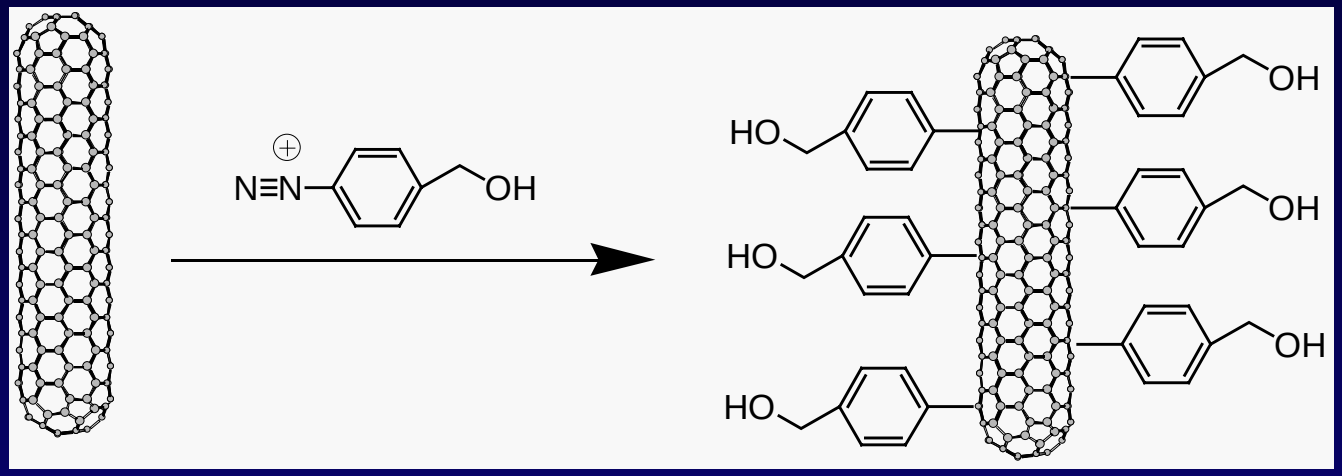
Courtesy of Prof. C. Lieber, Harvard



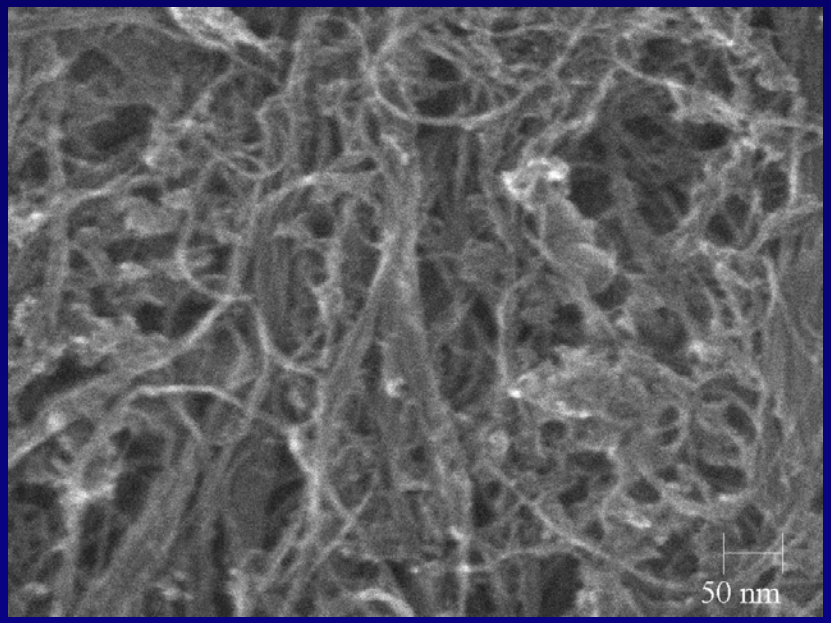


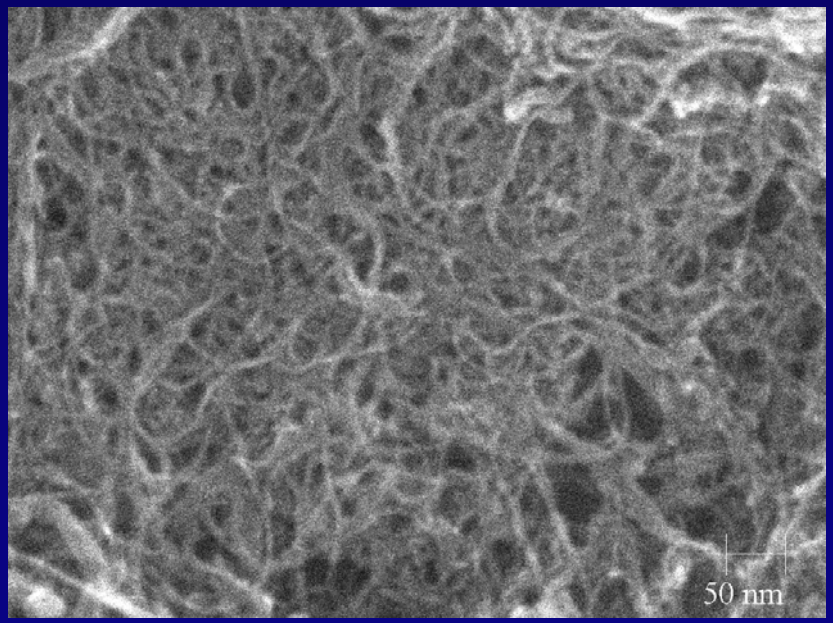


Functionalization and De-functionalization of CoMoCAT nanotubes



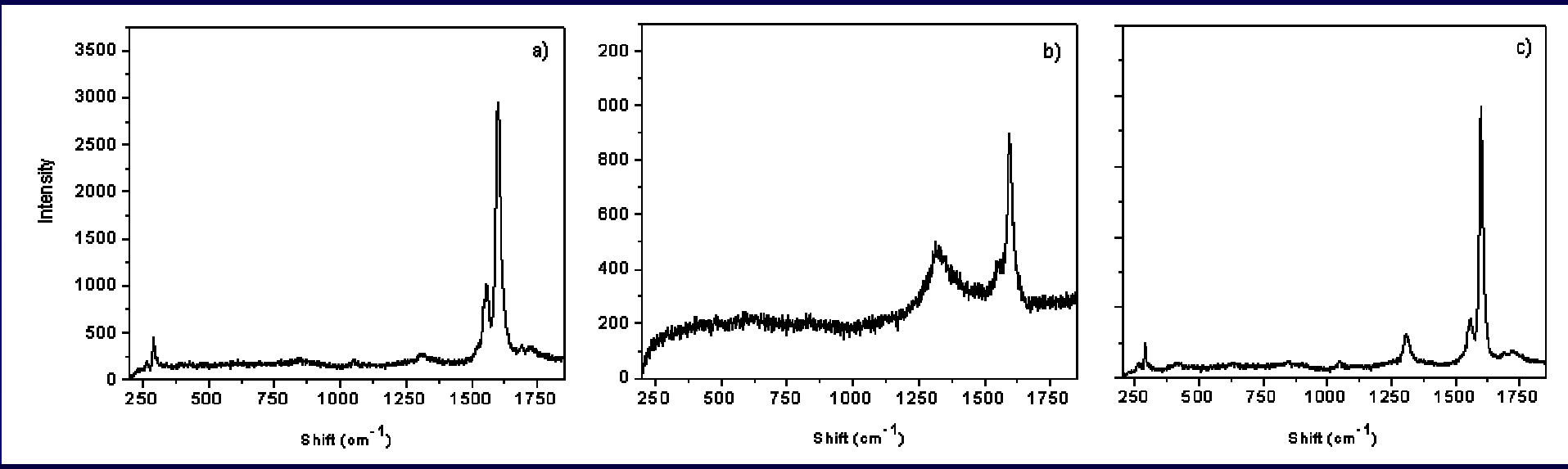
SWNT-HMA 1:4 ODCB





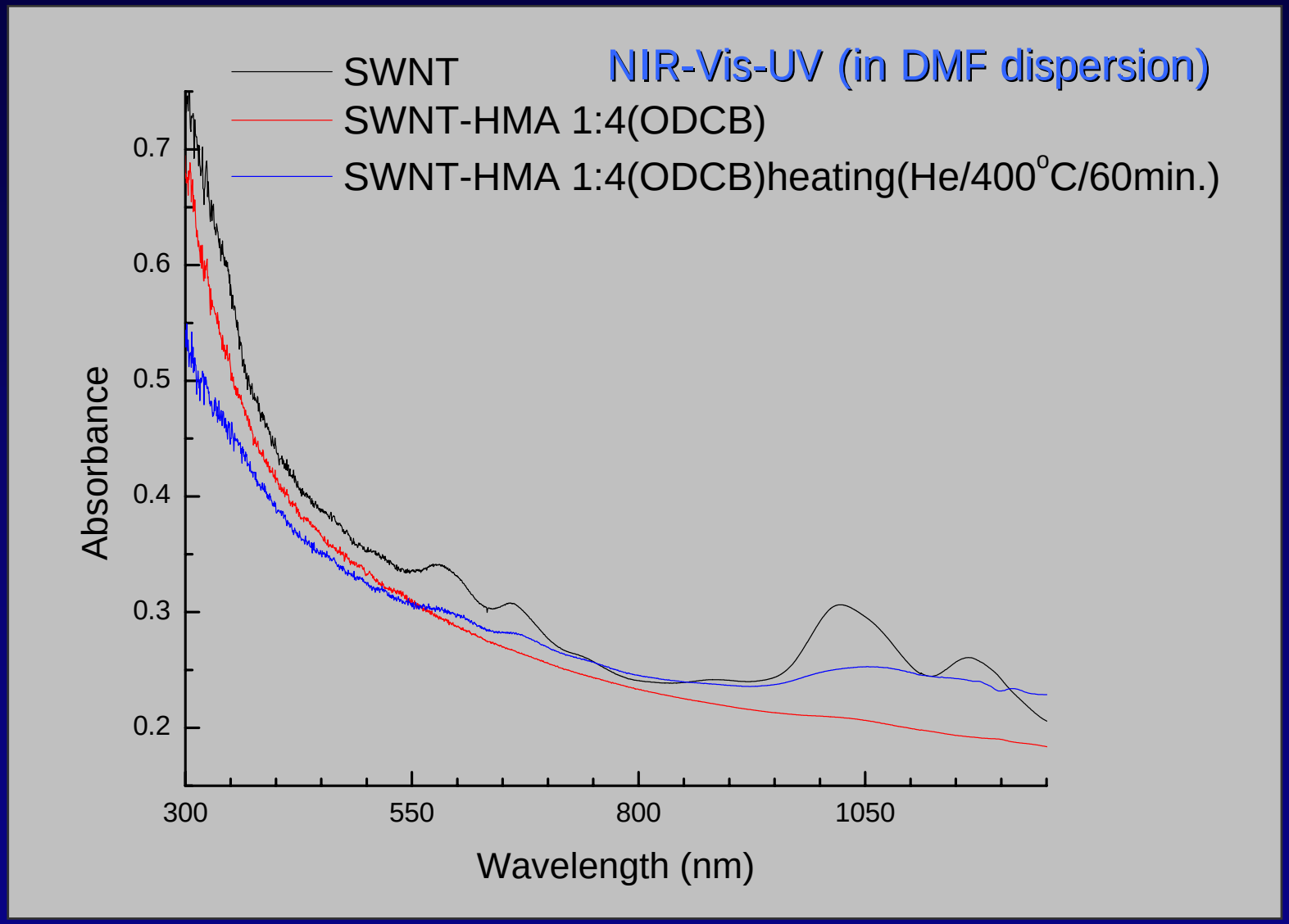
Functionalization and De-functionalization

Raman spectra (633 nm excitation)



a) Pristine nanotubes
b) Functionalized with 4-hydroxymethylaniline
c) De-functionalized by heating in He at 400C

Functionalization and De-functionalization



Conclusions

- Raman, NIR, PL, STM, TEM all agree that CoMoCAT samples have narrow distribution of diameters (with (6,5) the most abundant semiconducting)
- XPS, TGA, TPO all show high SWNT purity on these samples.
- Full SWNT characterization requires a combination of techniques.
- Relationship between aggregation state and spectral features still not fully understood for some techniques (Raman and optical absorption)
- Development of a Technique for Quantification of metallic/semiconducting ratio is needed.
- Quality assessment must focus on
  - Level of impurities (catalyst; other C)
  - Dispersibility
  - SWNT structures present in sample

Acknowledgements

- NASA Phase I SBIR
- NASA Phase II SBIR
- NSF Phase I SBIR
- DoE. Basic Energy Sciences (grant No. DE-FG03-02ER15345)
- National Science Foundation (grant No. CTS-0308619)
- OCAST

Web sites:

www.ou.edu/engineering/nanotube

www.swnano.com