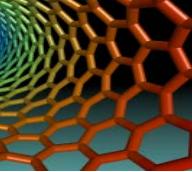


# Probing the underlying physics of nanoelectronics with Raman spectroscopy

Angela R. Hight Walker, Ph.D.

Physical Measurement Laboratory  
National Institute of Standards and Technology  
[angela.hightwalker@nist.gov](mailto:angela.hightwalker@nist.gov)



# New Group Formed at NIST

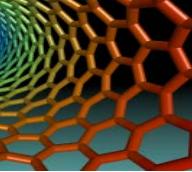


*Lead by Curt Richter*

## NANOELECTRONICS GROUP (683.04)

Conducts basic research to advance the optical and electrical measurement science infrastructure necessary for innovation in future nanoelectronic and thin-film devices, and their component materials.

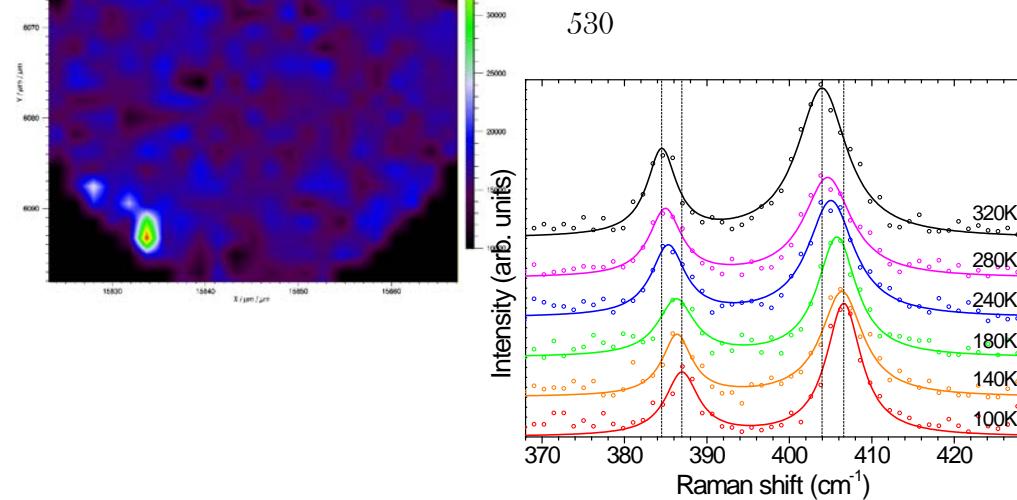
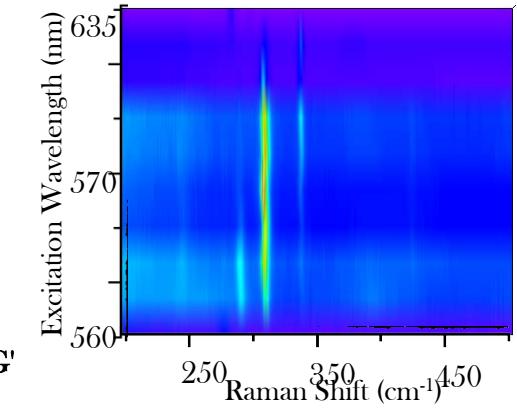
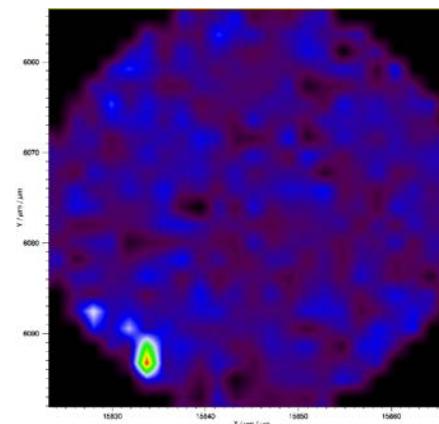
- **Pushes the frontiers of optical spectroscopies (e.g., Raman spectroscopy, spectroscopic ellipsometry, and infrared spectroscopy) and electrical measurements (e.g., magnetotransport, nanoelectronic test structure development, and temperature dependent current-voltage spectroscopy)**
- **Develops and advances novel measurements that combine and correlate optical and electrical methods such as internal photoemission, magneto-optical spectroscopy, and transient photocurrent spectroscopy.**

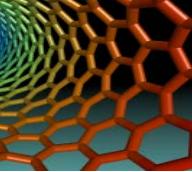


# Outline

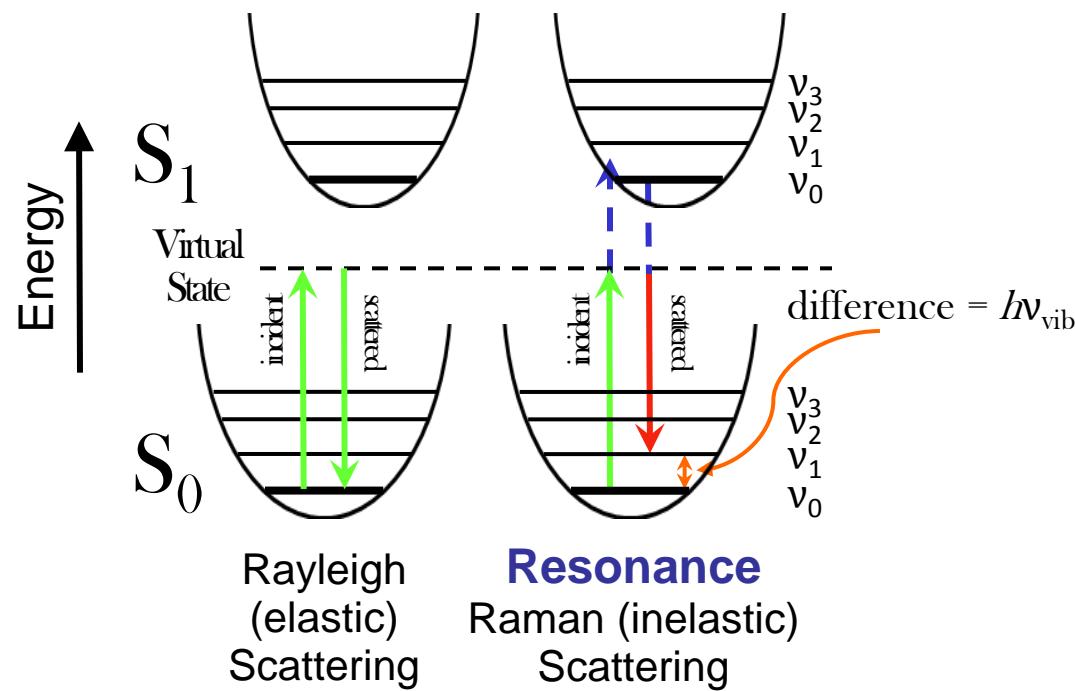
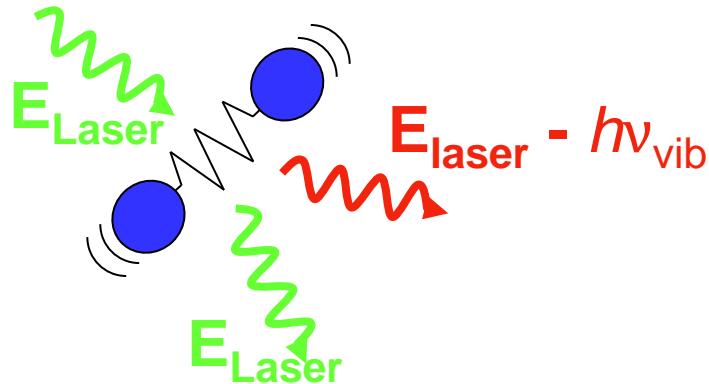
*Raman spectroscopy applied to*

- Carbon Nanotubes
- 2D Materials
  - Graphene
  - MoS<sub>2</sub>

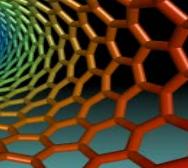




# The Raman Effect: Inelastic Scattering

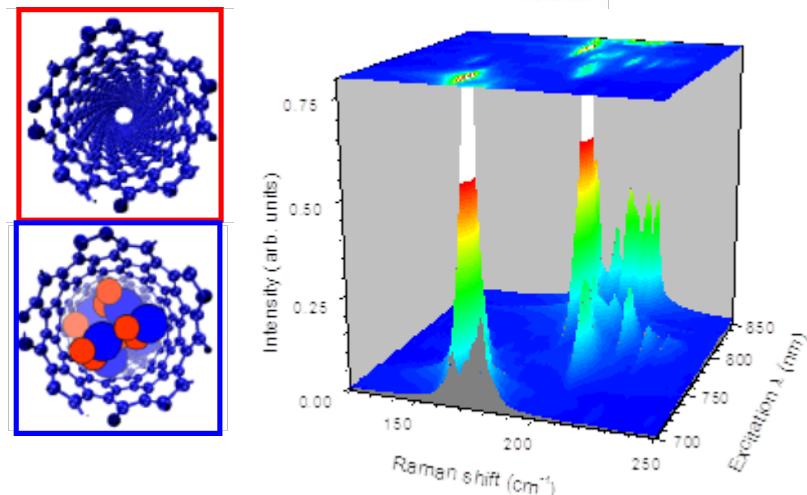
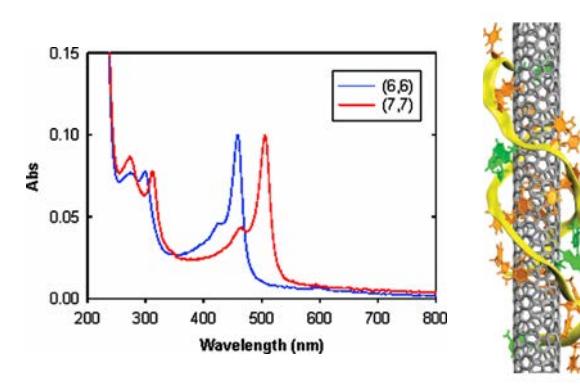


- Rapid
- Highly specific
- Non-destructive
- Rich
  - Layer number and orientation
  - Defects/Edges
  - Electron Phonon coupling
  - Temperature
  - Doping
  - Strain
  - Crystallographic orientation
  - Chemical functionalization



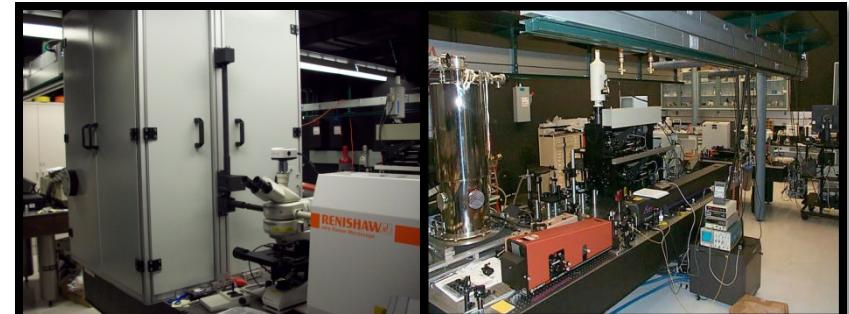
# Novel Measurement Methods

- Techniques enhanced by presence of the nano-object
- Very sensitive to carbon nanostructures, i.e. carbon nanotubes and graphene
- Unique capabilities spanning THz through NIR region



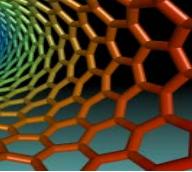
## Expertise and Resources

- Raman Spectroscopy
  - Triple-grating XY-800
  - Renishaw InVia Microscope
- Laser fluorescence spectroscopy
- Combined AFM-Raman imaging
- Surface-enhanced Raman spectroscopy (SERS)
- Tip-enhanced Raman spectroscopy (TERS)
- Multiple laser excitation
  - Argon ion (multiple discrete lines), Ti:Sapphire (tunable), 633 nm HeNe, 785 nm diode, Dye lasers (tunable)
- Cryostats : 4 K - 400 K
- Environmental cell



ACS Nano 2011 5, 5 3943

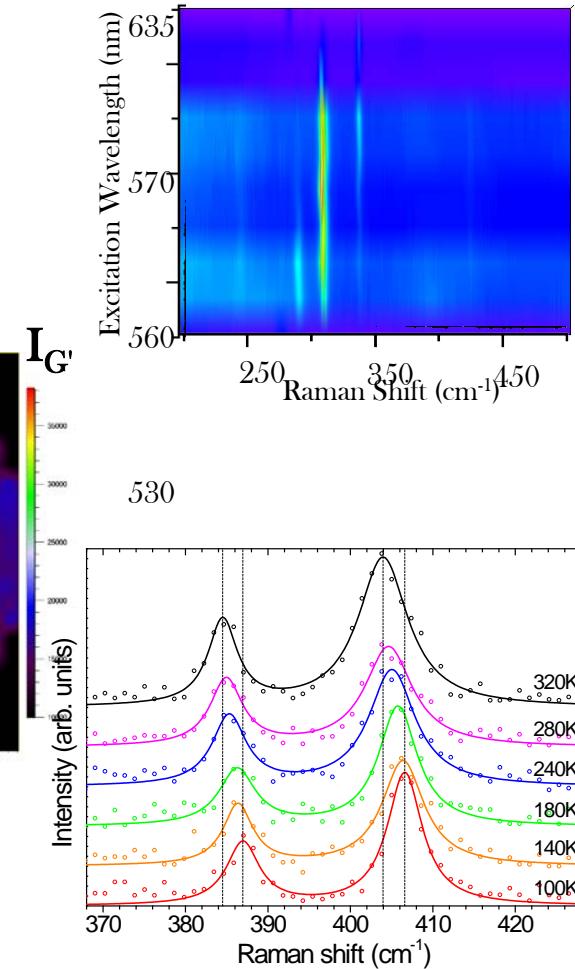
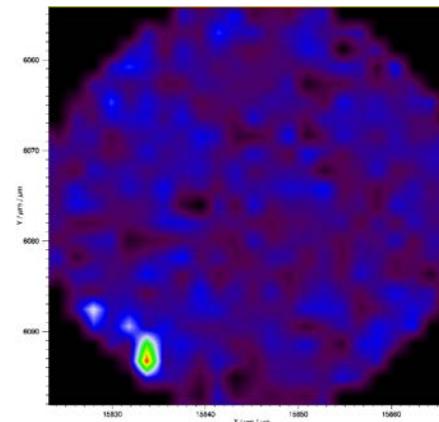
J. Am. Chem. Soc., 2011, 133 (33), pp 12998–13001

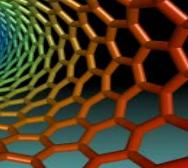


# Outline

*Raman spectroscopy applied to*

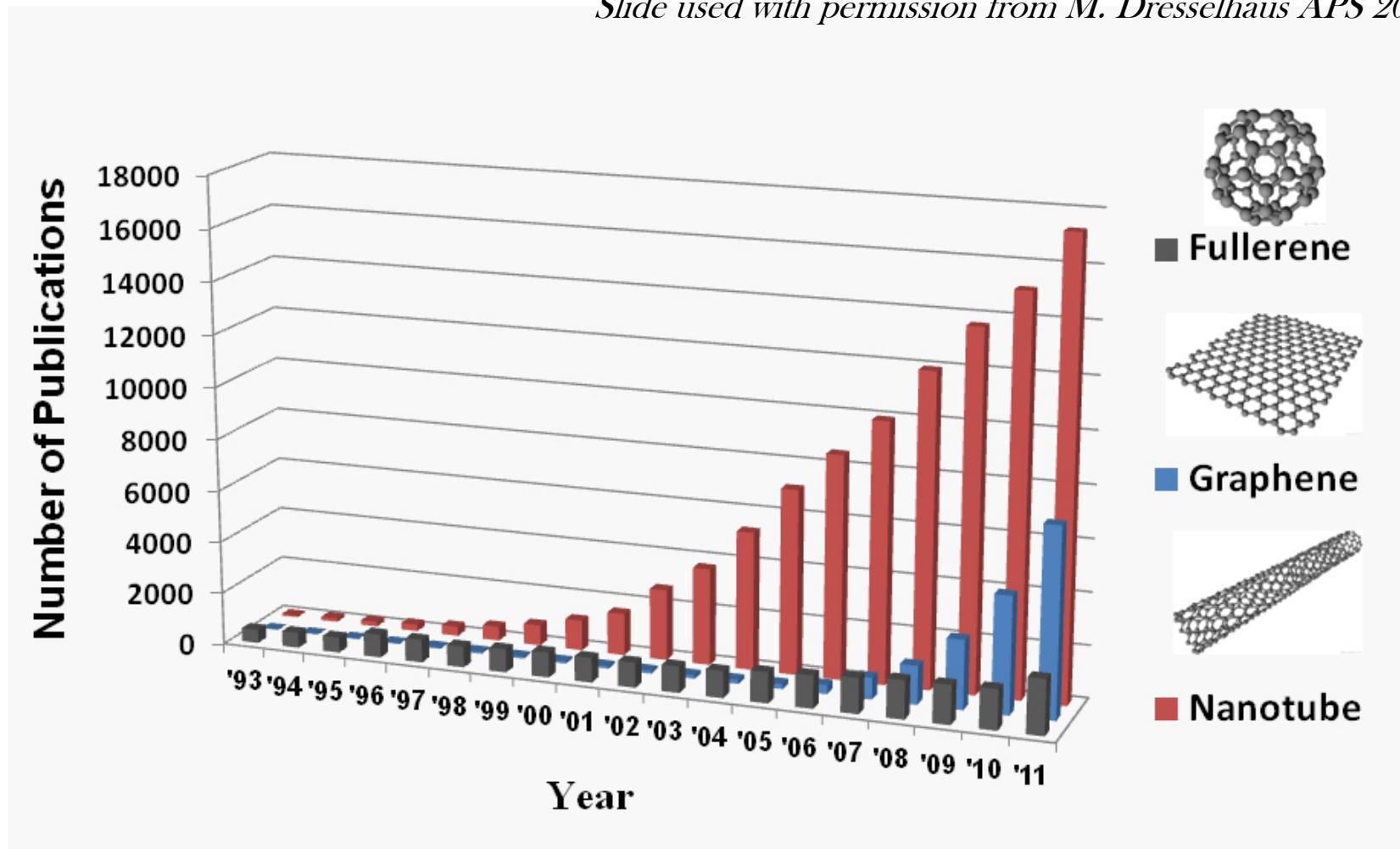
- Carbon Nanotubes
- 2D Materials
  - Graphene
  - MoS<sub>2</sub>



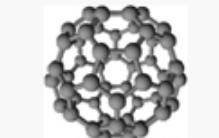


# Publications per year

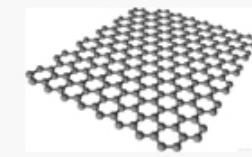
Slide used with permission from M. Dresselhaus APS 2013



Data extracted from the Web of Knowledge (Science Citation Index) searching for the words fullerene, nanotube, and graphene.



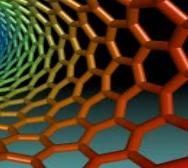
■ Fullerene



■ Graphene



■ Nanotube



# Nanoelectronics

nature  
nanotechnology

LETTERS

PUBLISHED ONLINE: 28 OCTOBER 2012 | DOI: 10.1038/NNANO.2012.189

The New York Times Technology | Personal Tech | Business Day

## Bits

OCTOBER 28, 2012, 2:00 PM | 45 Comments

### I.B.M. Reports Nanotube Chip Breakthrough

By JOHN MARKOFF

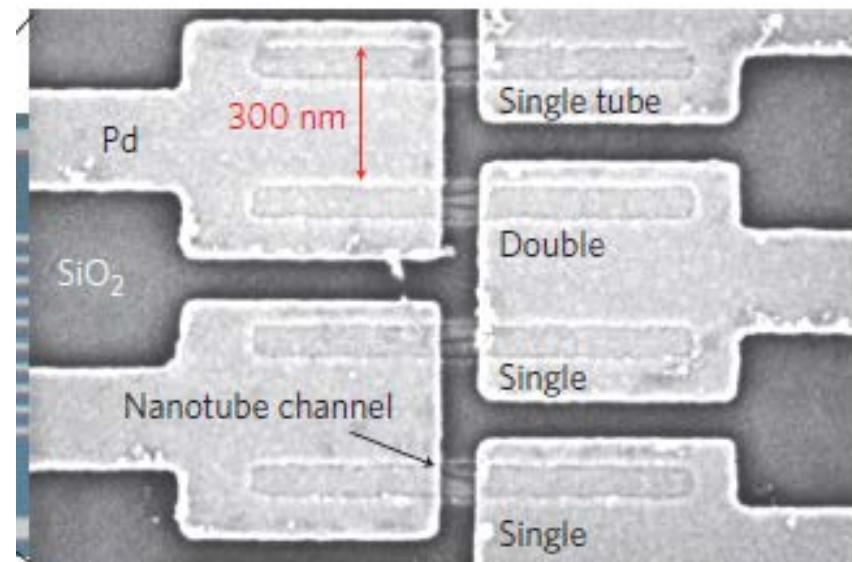
SAN FRANCISCO — [I.B.M.](#), scientists are reporting progress in a chip-making technology that is likely to ensure that the basic digital switch at the heart of modern microchips will continue to shrink for more than a decade.

The advance, first described in the journal *Nature Nanotechnology* on Sunday, is based on carbon nanotubes — exotic molecules that have long held out promise as an alternative to silicon from which to create the tiny logic

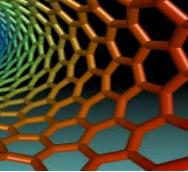


I.B.M. Research

The face of an I.B.M. research scientist, Hongsik Park, is reflected in a wafer used to make microprocessors.

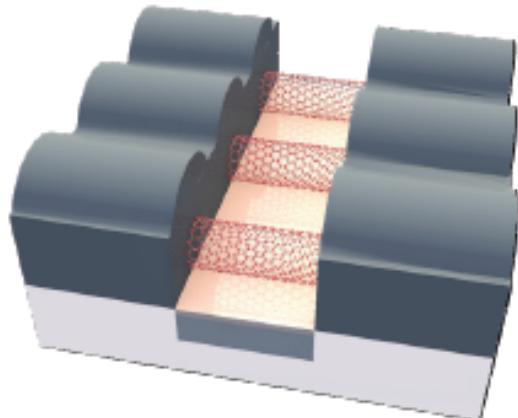


NIST



# Recent Workshop

## Carbon N<sub>T</sub> Digital Electronics WORKSHOP



### Purpose:

To review and discuss the current status and potential benefits of carbon nanotubes in digital electronic applications.

### Who will attend (Invitation only):

- Top researchers in the field from academia, government, and industry.
- Program managers and other colleagues from relevant government agencies.

#### Date:

Thursday, September 6, 2012

#### Location:

NIST  
100 Bureau Drive  
Gaithersburg, MD 20899

#### Registration:

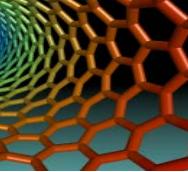
[http://www.nist.gov/pml/div683/cnt\\_workshop.cfm](http://www.nist.gov/pml/div683/cnt_workshop.cfm)

No registration fees

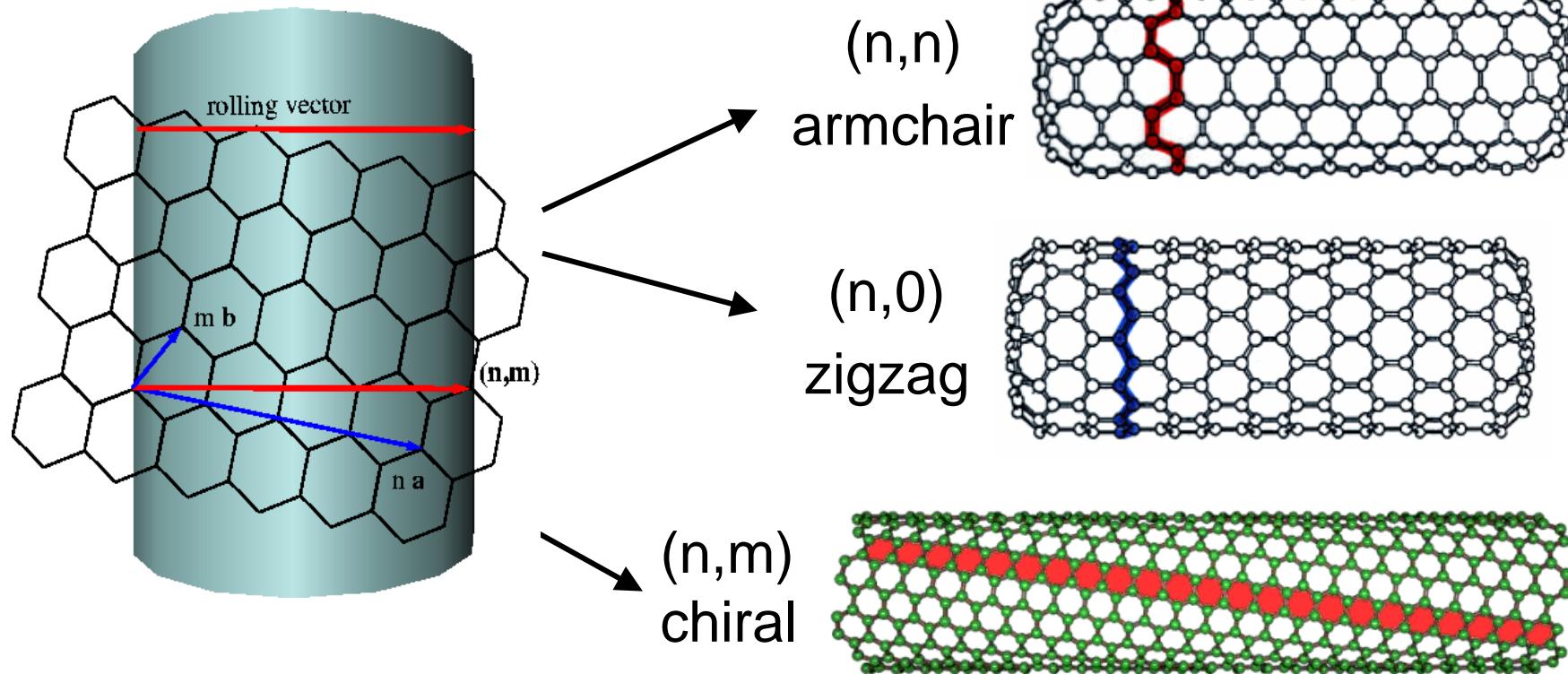
Coffee and lunch provided

#### Lodging:

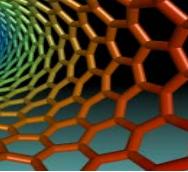
Block of rooms reserved for 9/5 and 9/6 at Hilton



# Single-Wall Carbon Nanotubes

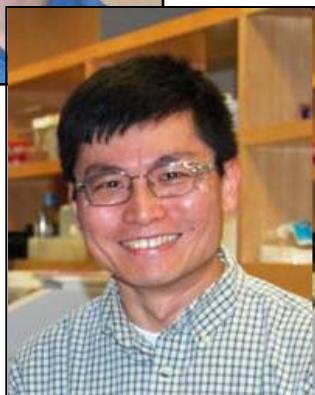


Roll up vector determines physical properties,  
electronic nature and surface interactions.



# NIST SWCNT Team

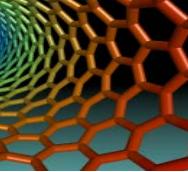
## Fundamental Metrology for Carbon Nanotube Science and Technology



Identify the fundamental properties of the  
nanomaterials



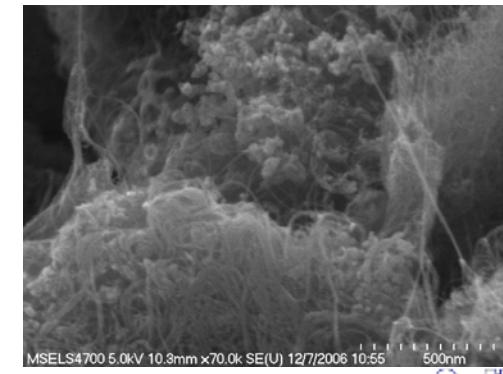
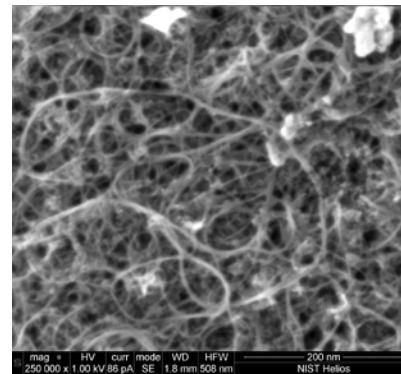
Isolate the nanomaterial for study

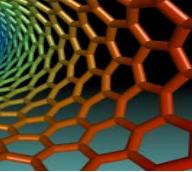


# Polydispersity Problem

**ALL SAMPLES  
are DIFFERENT**

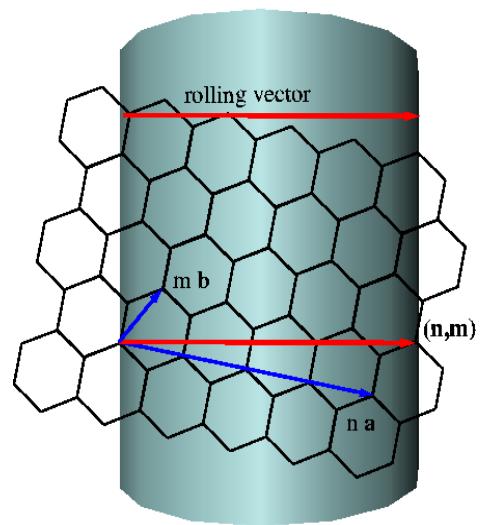
**SWCNT length  
distribution, powder  
morphology,  
impurity content all  
vary batch to batch  
(or even within a  
batch) and across  
manufacturers.**



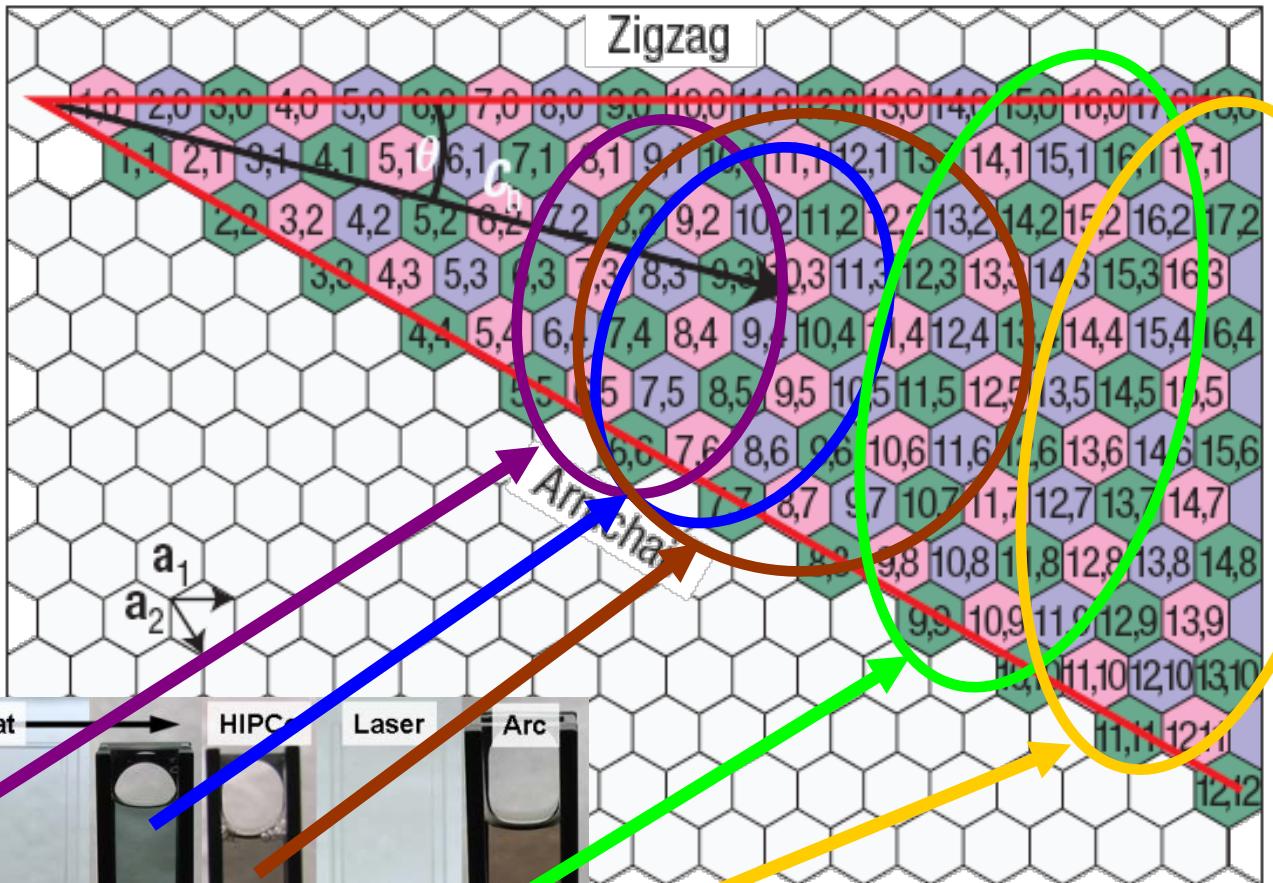
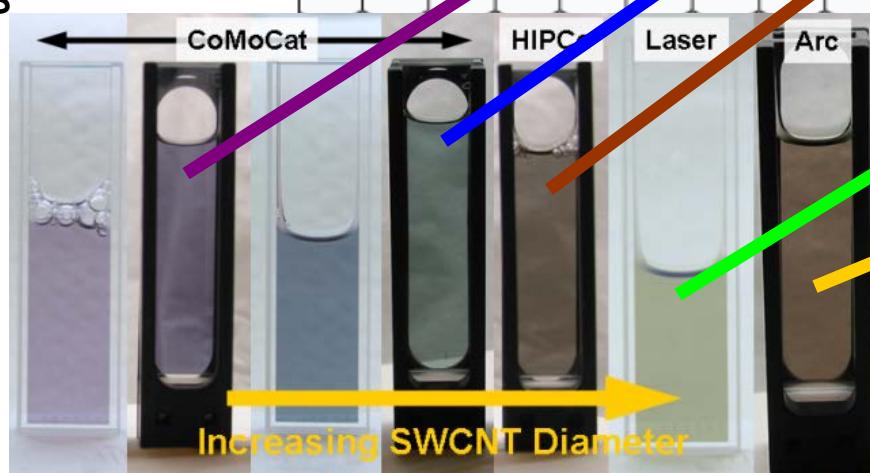


# Polydispersity

*Synthesis techniques produce varying SWCNT distributions*



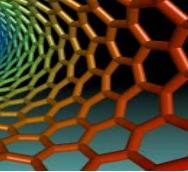
chiral vector  
determines physical  
properties



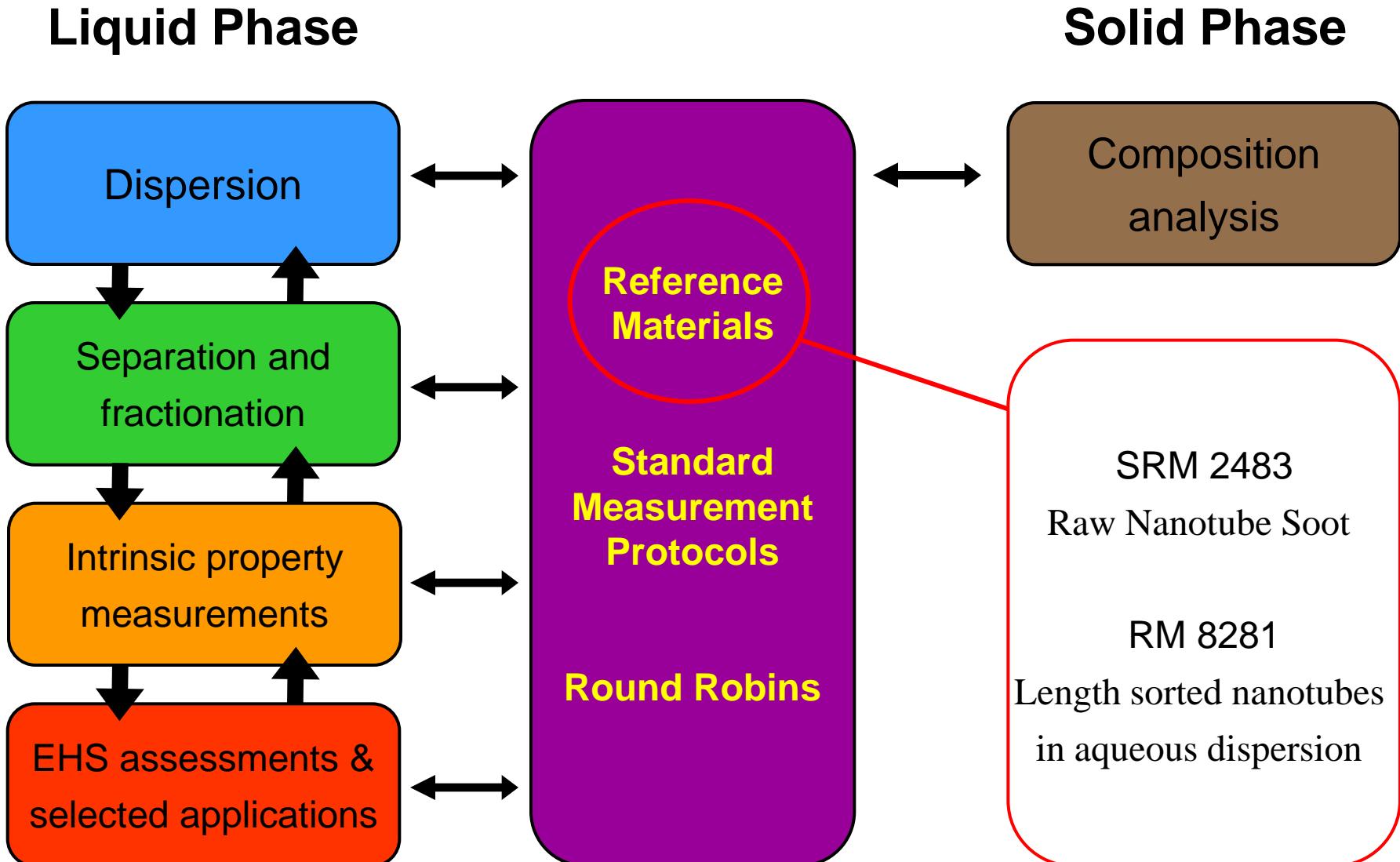
Hersam et al., Nature Nanotech 2008

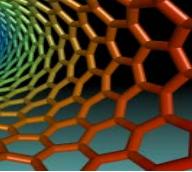
green: metallic;

Pink, Purple: Semi-conducting



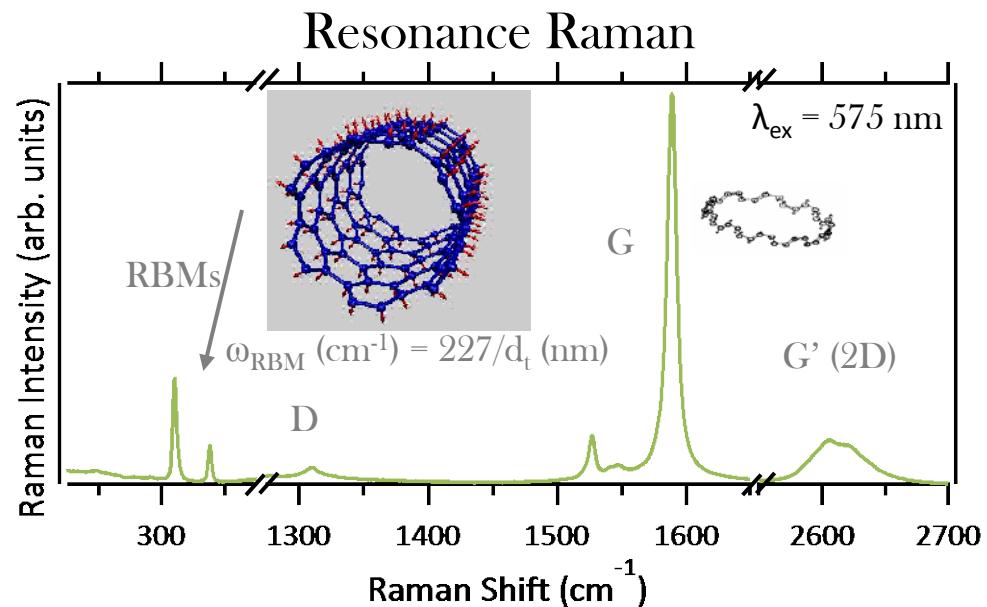
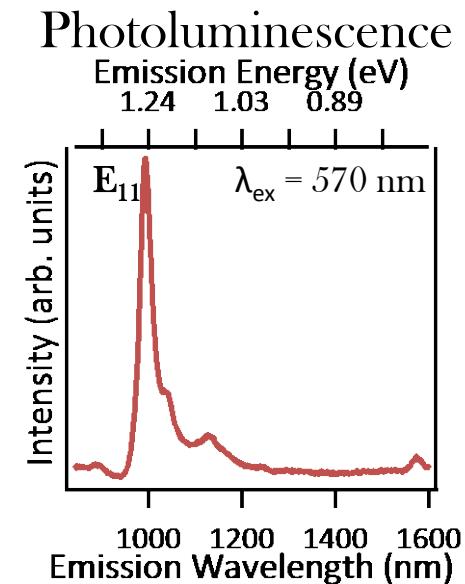
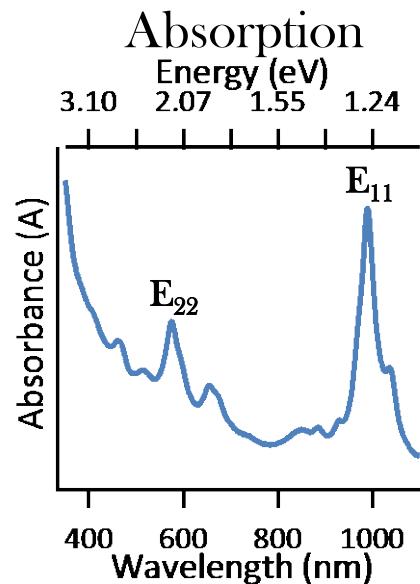
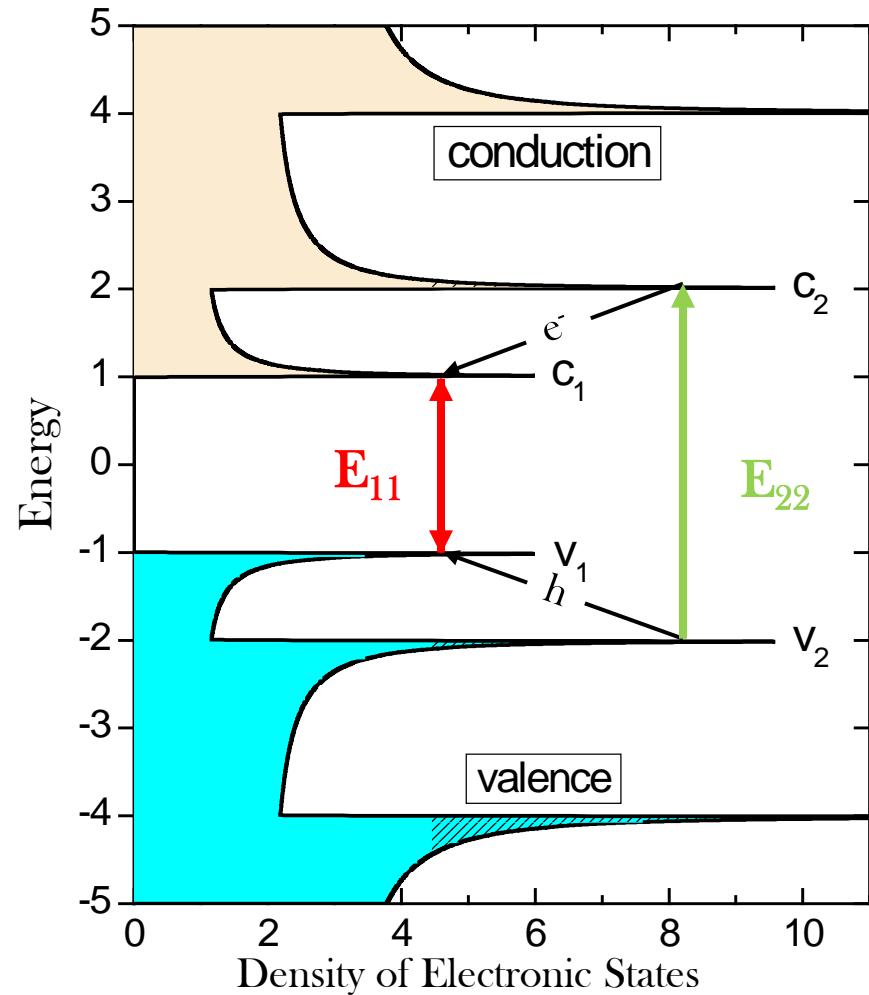
# Nanotube Metrology Program

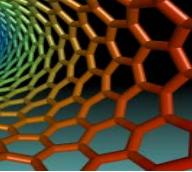




# Optical Properties of SWCNTs

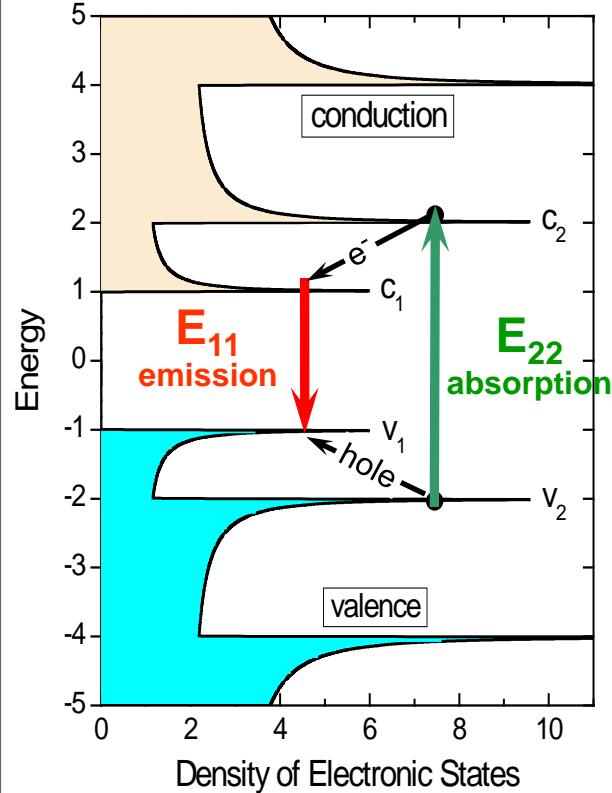
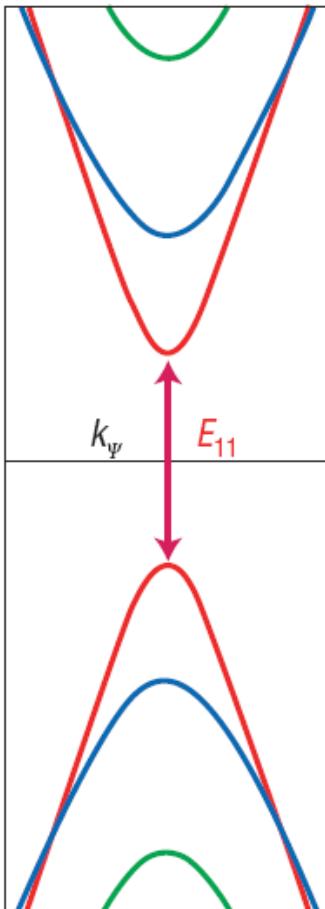
Optical properties of SWCNTs arise from van Hove singularities in 1-D density of states



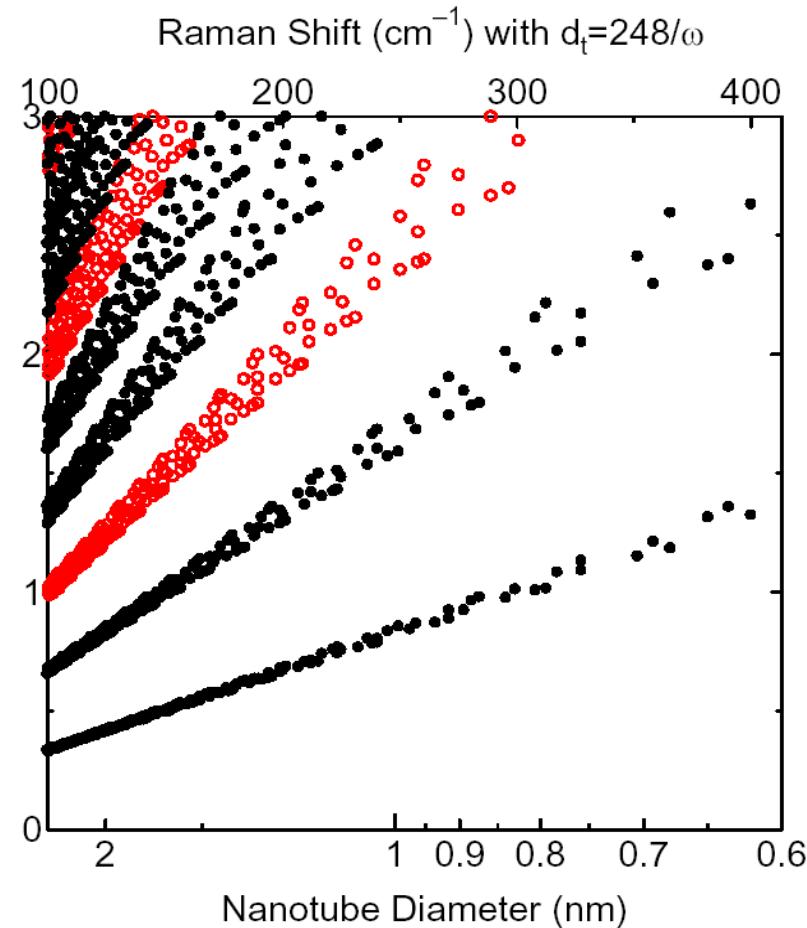


# Electronic Structure of SWCNTs

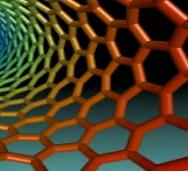
## 1D Density of States – van Hove singularities



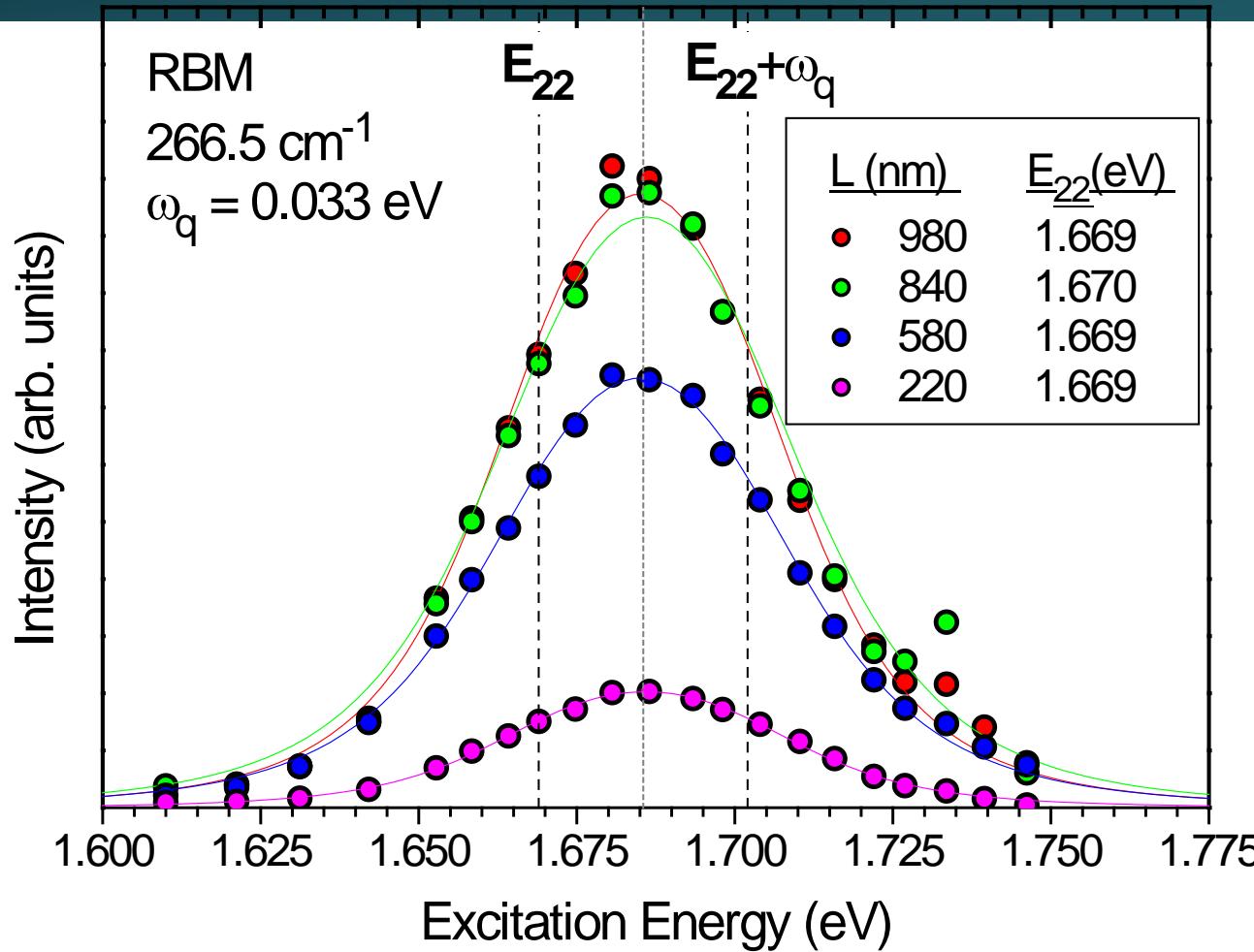
## Katuara Plot



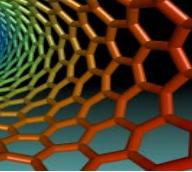
van Hove Singularities in density of states → resonance Raman.  
Resonance energy with Raman peak position gives unique (n,m)



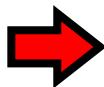
# Resonance Excitation



$$I_s \propto \sum_{j,k} \left| \frac{\langle 0 | V_{opt} | j \rangle \langle j, N \pm 1 | V_{ex-ph} | k, N \rangle \langle k | V_{opt} | 0 \rangle}{(E_k - E_{ii} + i\Gamma)(E_j - E_q - E_{ii} + i\Gamma)} \right|^2$$



# Separation for various diameters / synthesis

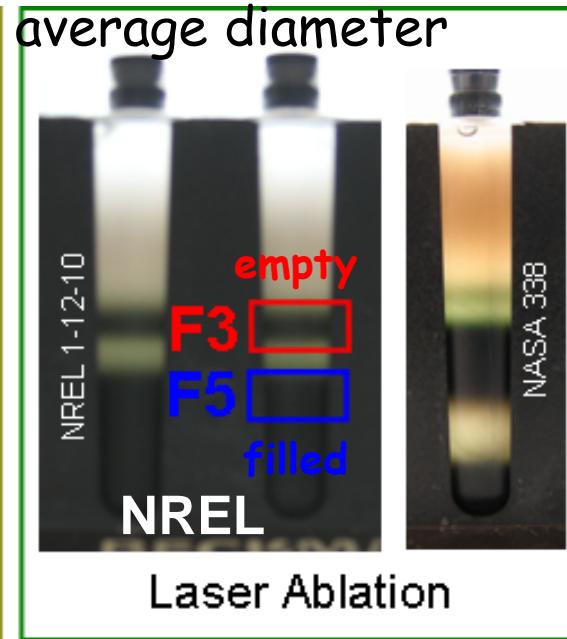


<diam>

0.8 nm

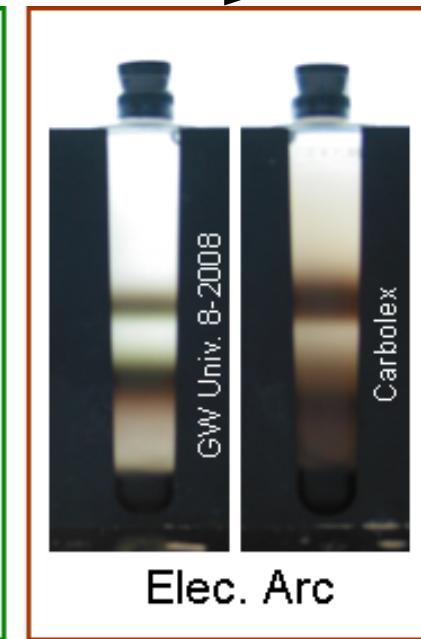


1.0 nm



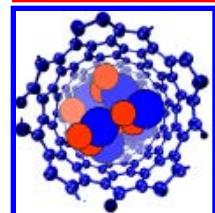
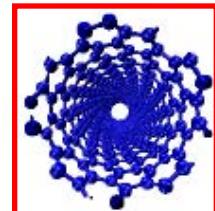
NREL  
Laser Ablation

1.3 nm



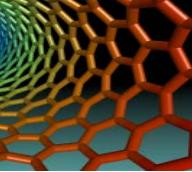
Elec. Arc

1.5 nm

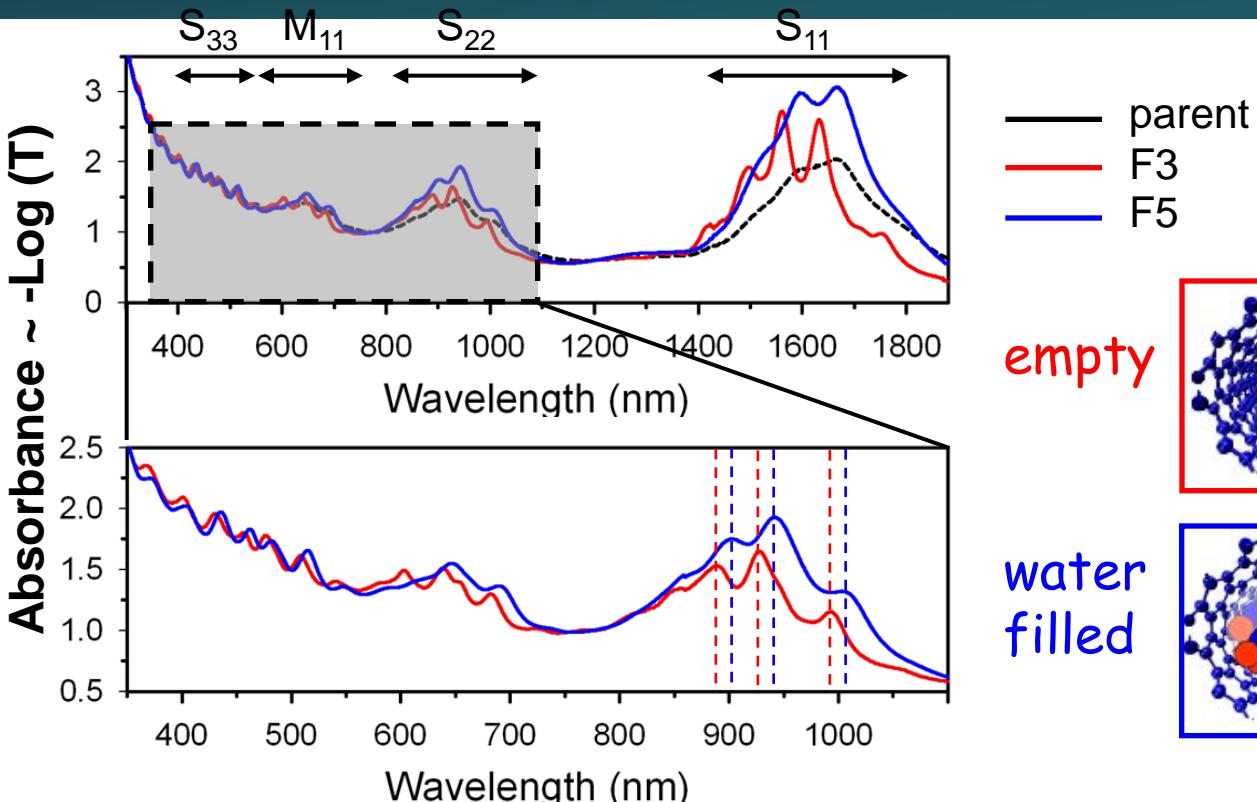
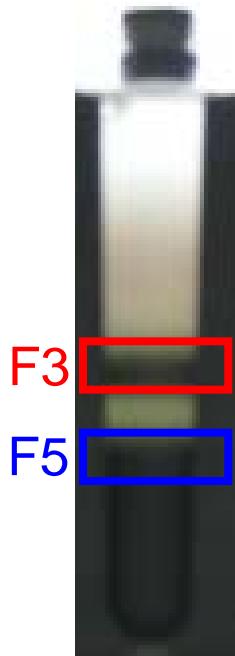


1. Separation into 2 distinct bands, increase with diameter
2. Lower band progresses further down with diameter
3. Motion of nanotube bands through medium is progressive
  - robust results across various synthesis methods
  - consistent with endohedral water-filling

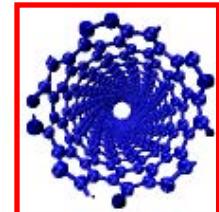
\*CoMoCat excluded



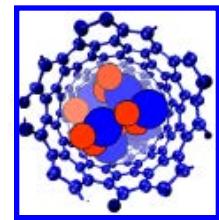
# Optical Absorption: UV-Vis-NIR



empty



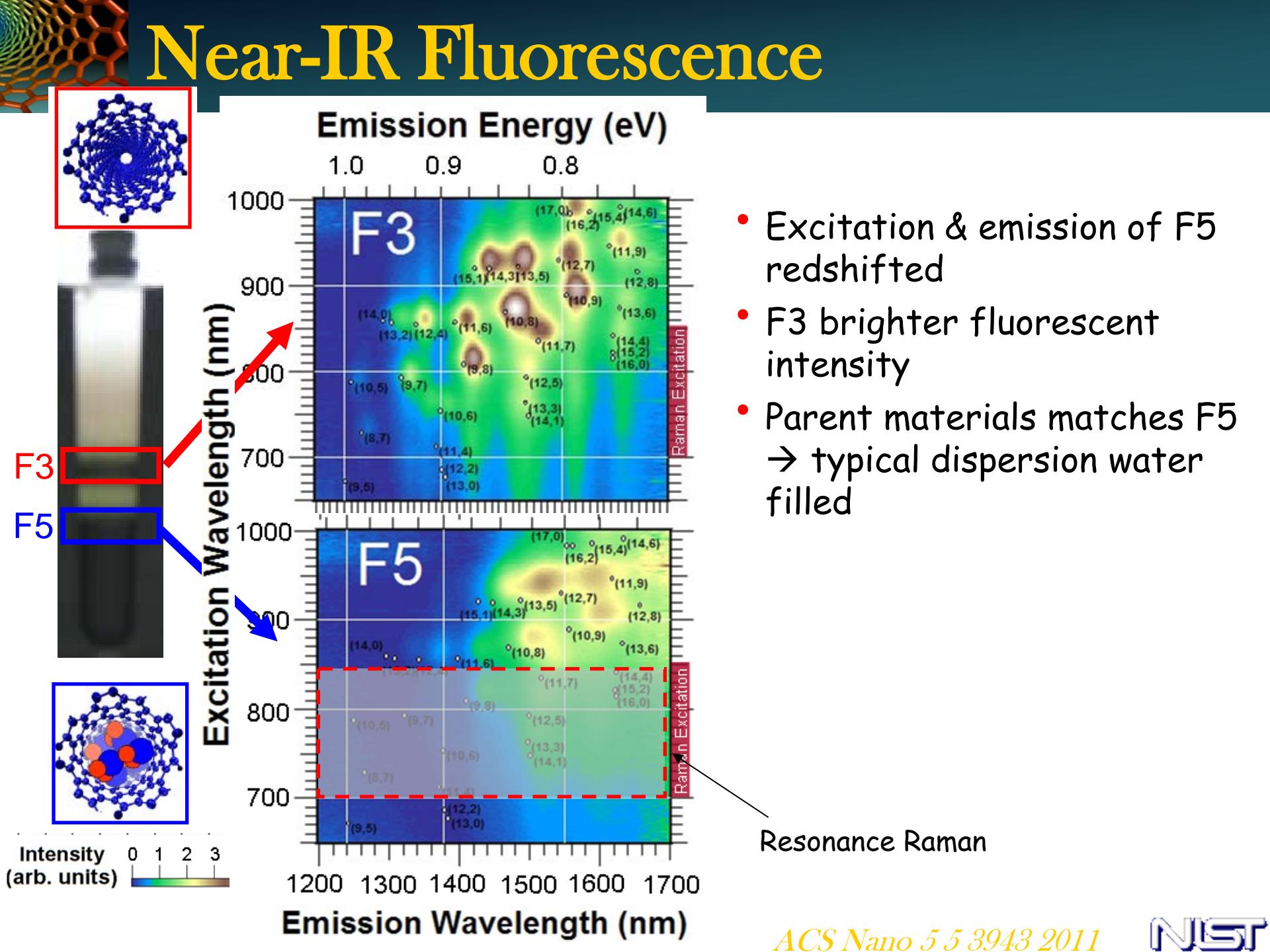
water filled

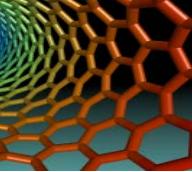


- Peaks **redshifted & broadened** in F5 for all excitonic bands, including metallic
- Similar diameter distribution in two bands
- Spectral weight of F5 comparable to or larger than F3

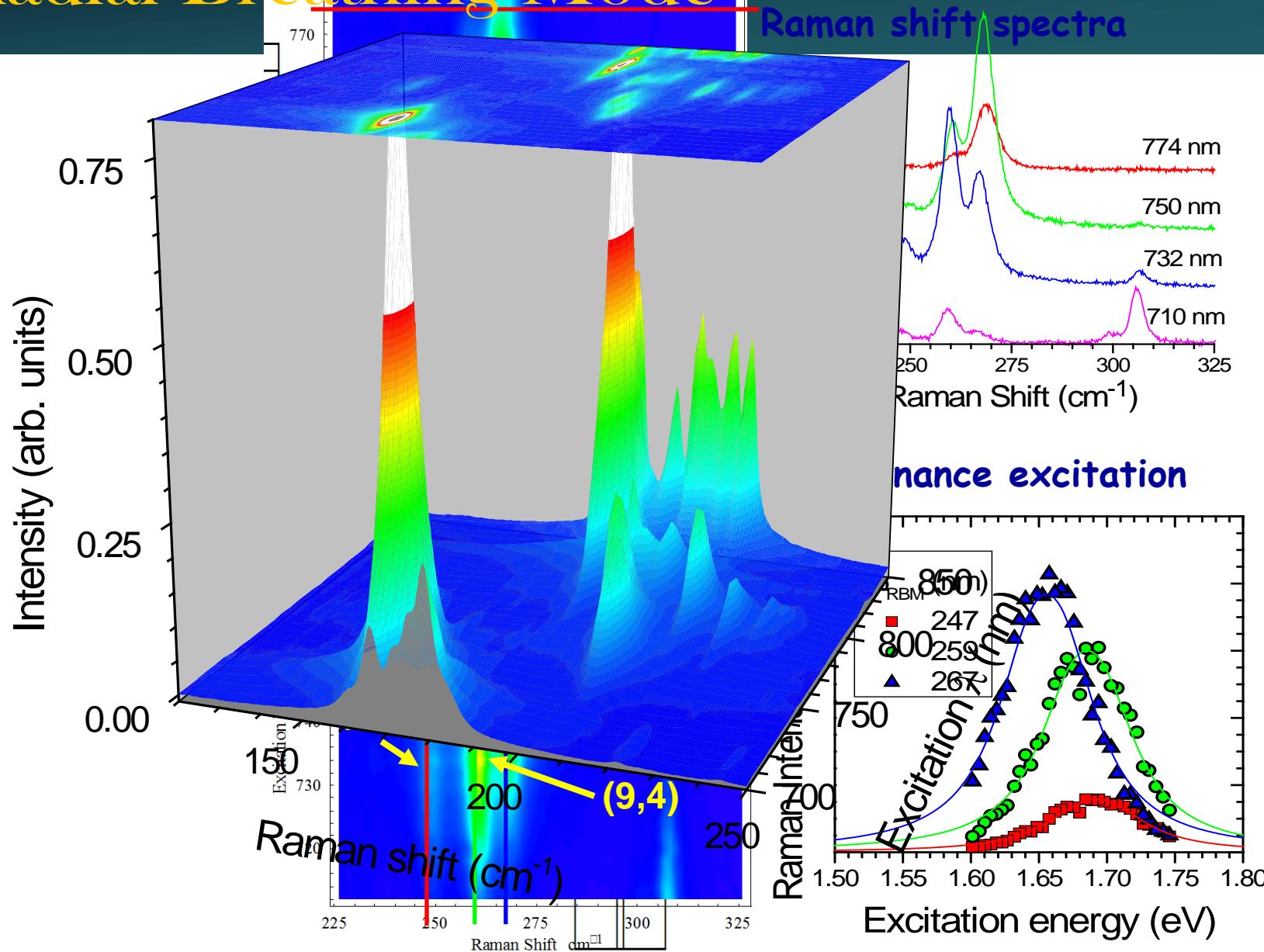
F5 **not** an aggregated state of F3 → filled

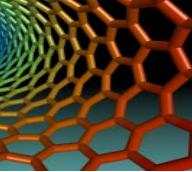
# Near-IR Fluorescence



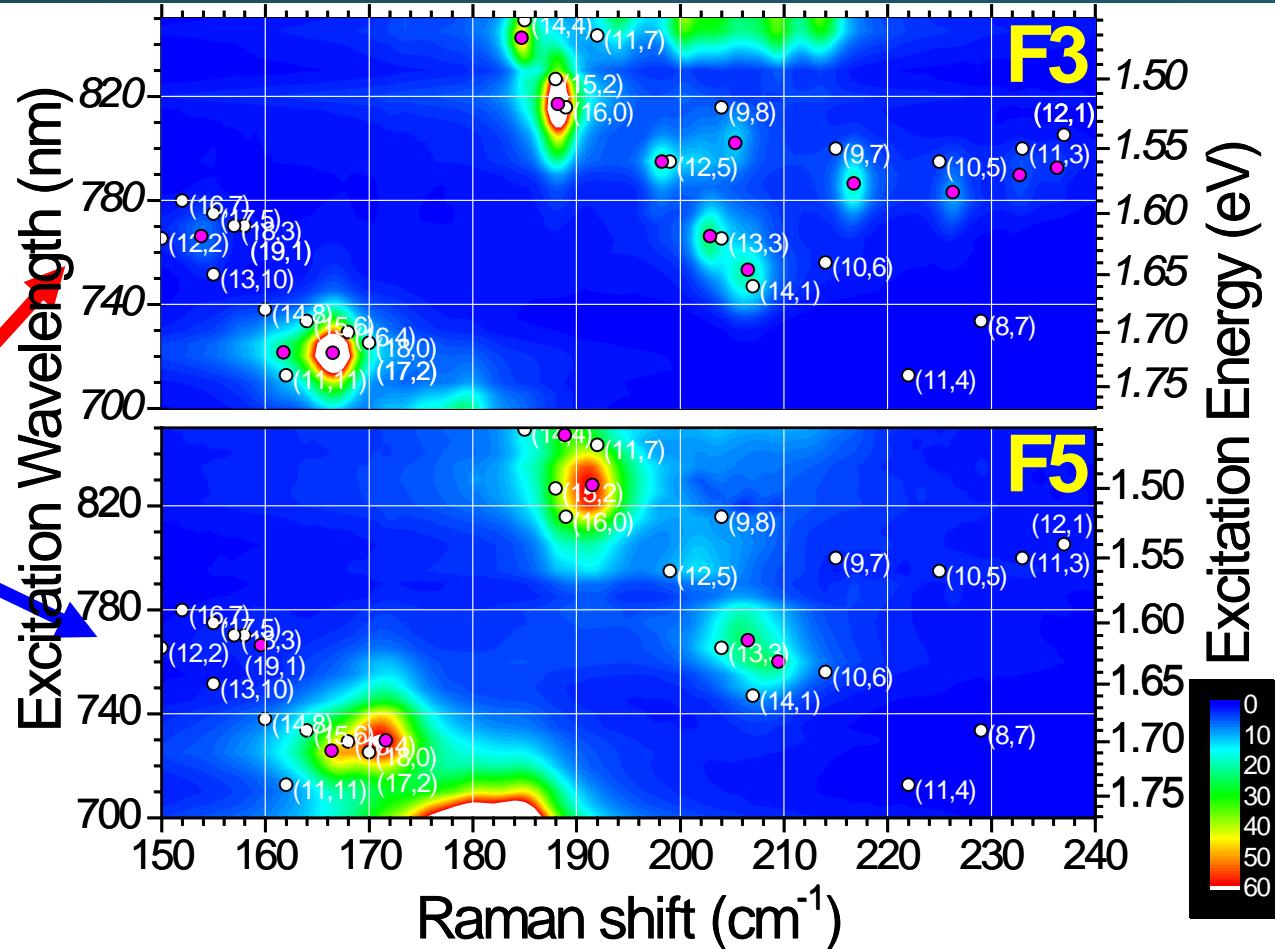
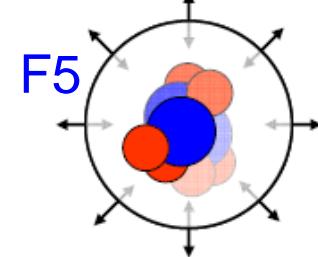
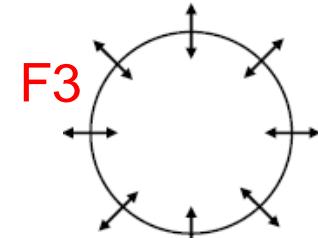
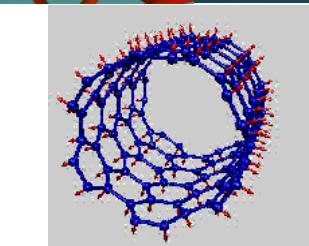


# Radial Breathing Mode

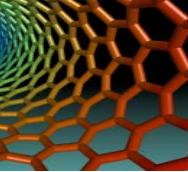




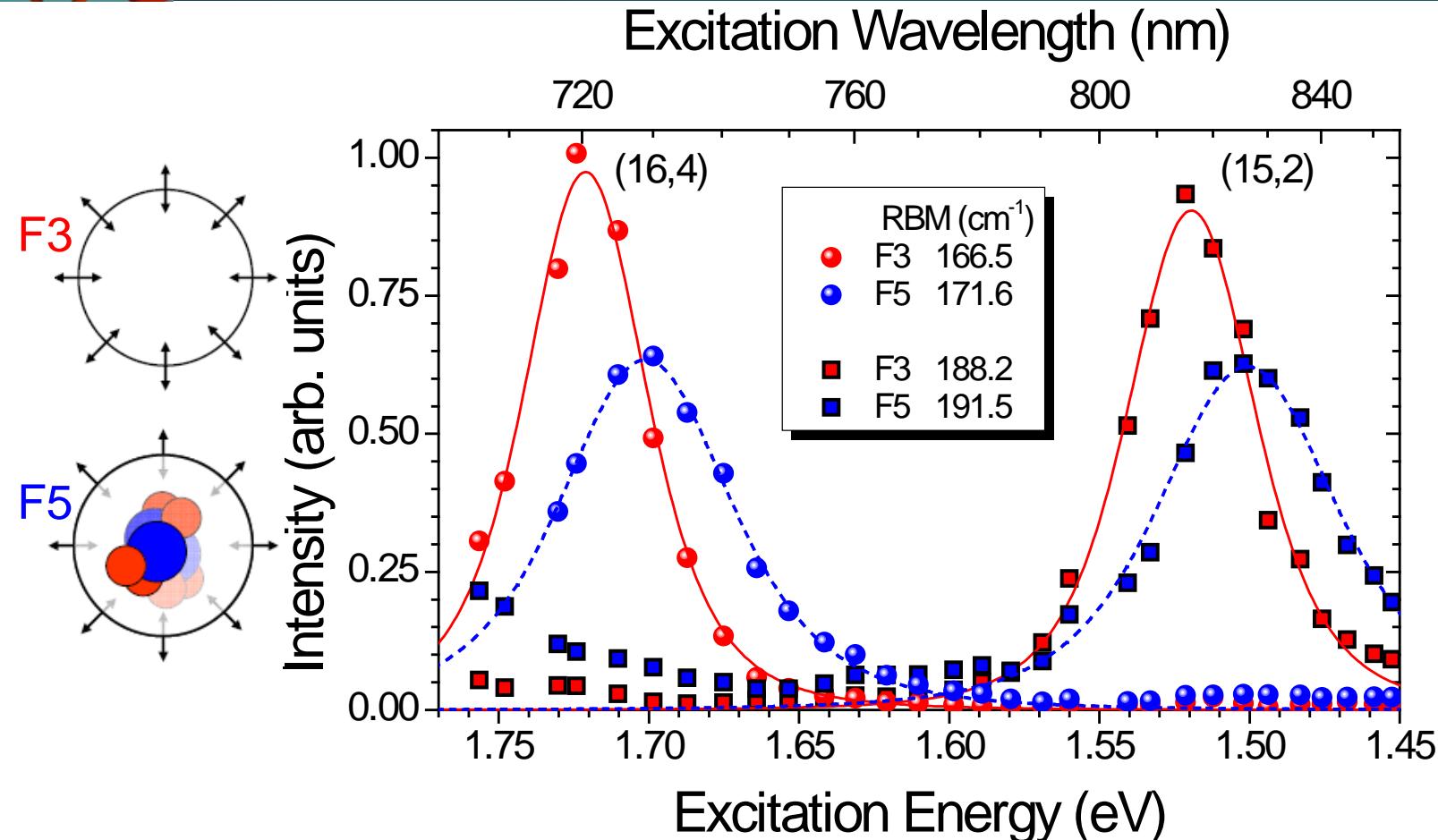
# Radial Breathing Modes (RBMs)



- Both semiconducting (S22) & metallic (M11) SWCNTs in resonance
- Excitation energies redshift in F5 (filled)
- RBM phonon frequencies harden (higher energy) with filling

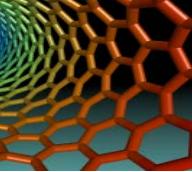


# Excitation Profiles of RBMs

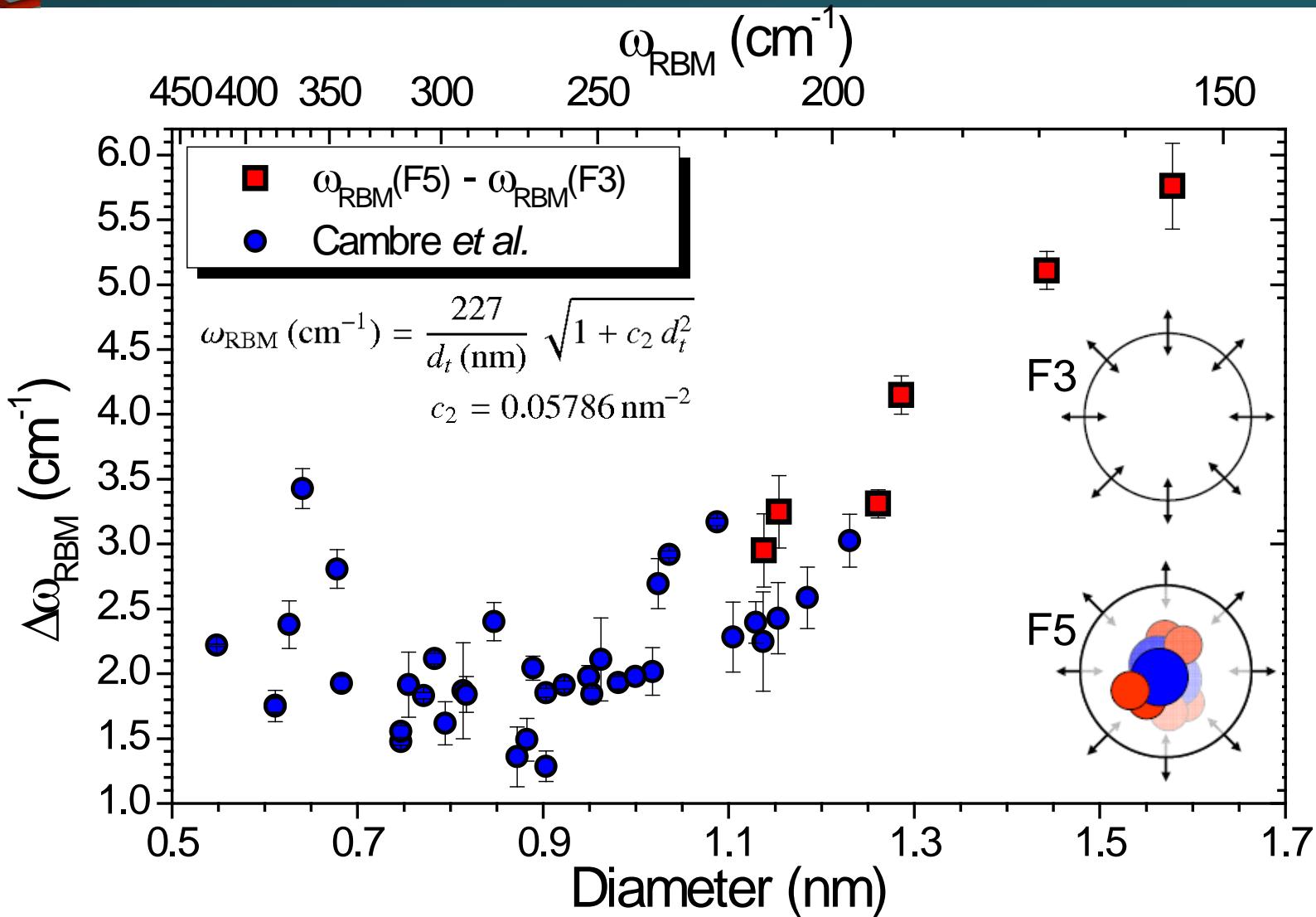


$$I_s \propto \sum_{j,k} \left| \frac{\langle 0 | V_{opt} | j \rangle \langle j, N \pm 1 | V_{ex-ph} | k, N \rangle \langle k | V_{opt} | 0 \rangle}{(E_k - E_{ii} + i\Gamma)(E_j - E_q - E_{ii} + i\Gamma)} \right|^2$$

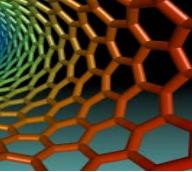
Excitations for F5 (filled) are red-shifted and broadened



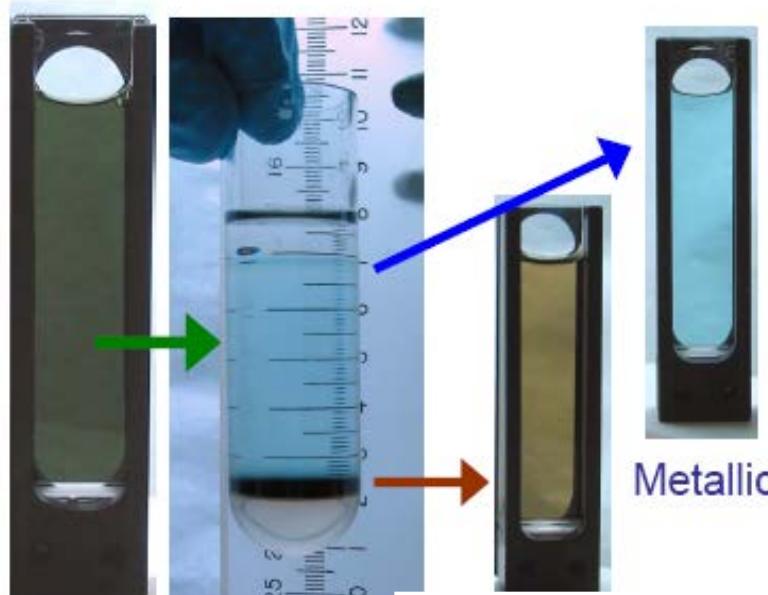
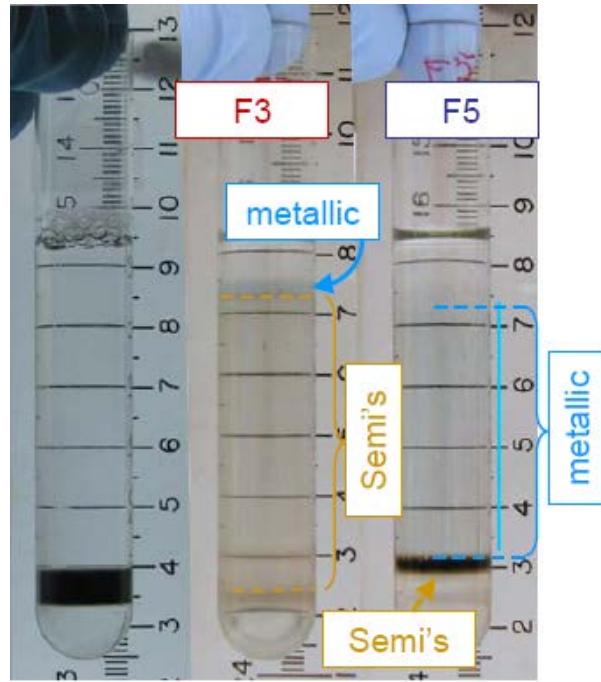
# Raman RBM Shift



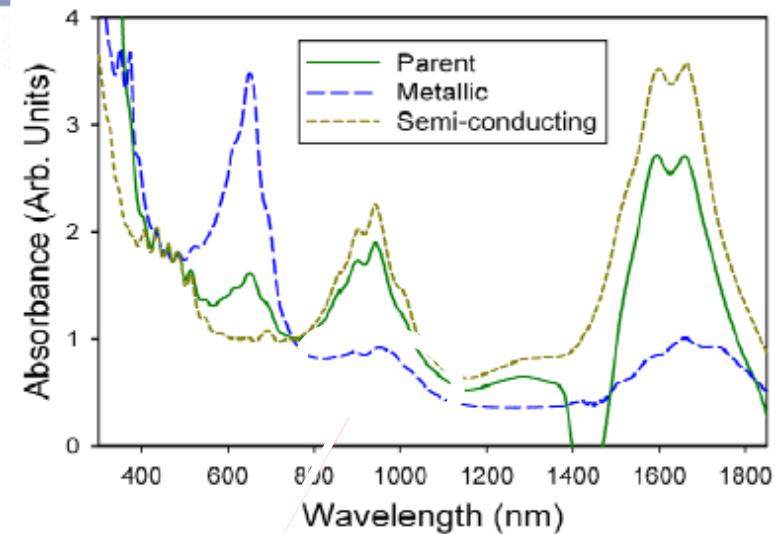
monotonic increase of hardening with increasing diameter

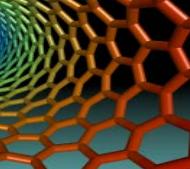


# Separation by Electronic Type



- Subsequent processing and separation by electronic type
- F5 (filled) easier to separate into semi-conducting & metallic





# DNA Dispersions of Carbon Nanotubes

nature

Vol 460 | 9 July 2009 | doi:10.1038/nature08116

LETTERS

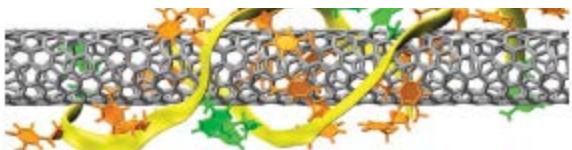
## DNA sequence motifs for structure-specific recognition and separation of carbon nanotubes

Xiaomin Tu<sup>1</sup>, Suresh Manohar<sup>2</sup>, Anand Jagota<sup>2,3</sup> & Ming Zheng<sup>1</sup>

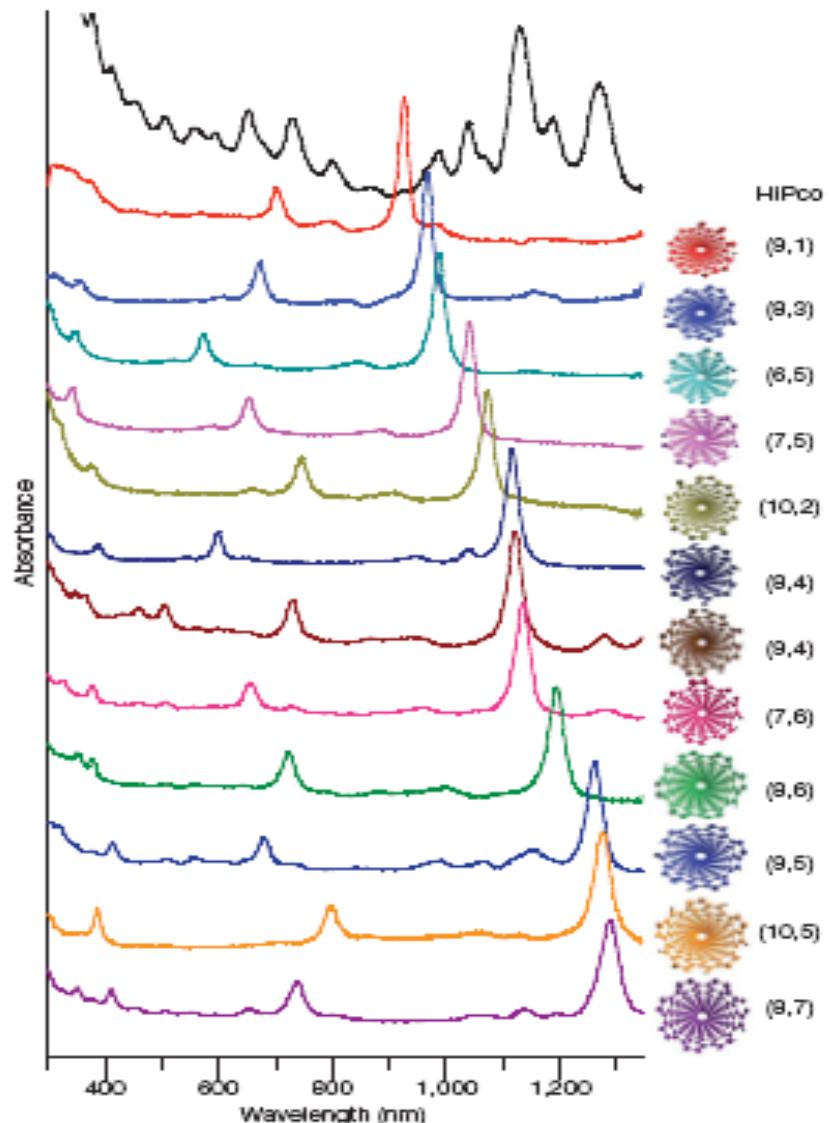
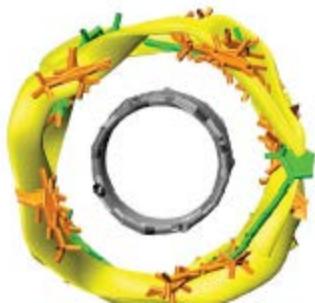
Table 1 | DNA sequence versus SWNT chirality

Chirality (n,m)	Sequences
(9,1)	(TCC) <sub>10</sub> , (TGA) <sub>10</sub> , (CCA) <sub>10</sub>
(8,3)	(TTA) <sub>4</sub> TT, (TTA) <sub>3</sub> TTGTT, (TTA) <sub>5</sub> TT
(6,5)	(TAT) <sub>4</sub> , (CGT) <sub>3</sub> C
(7,5)	(ATT) <sub>4</sub> , (ATT) <sub>4</sub> AT
(10,2)	(TATT) <sub>2</sub> TAT
(8,4)	(ATTT) <sub>3</sub>
(9,4)	(GTC) <sub>2</sub> GT, (CCG) <sub>4</sub>
(7,6)	(GTT) <sub>3</sub> G, (TGT) <sub>4</sub> T
(8,6)	(GT) <sub>6</sub> , (TATT) <sub>3</sub> T, (TCG) <sub>10</sub> , (GTC) <sub>3</sub> , (TCG) <sub>2</sub> TC, (TCG) <sub>4</sub> TC, (GTC) <sub>2</sub>
(9,5)	(TGTT) <sub>2</sub> TGT
(10,5)	(TTTA) <sub>3</sub> T
(8,7)	(CCG) <sub>2</sub> CC

DNA sequences enabling chromatographic purification of single chirality semiconducting SWNTs.

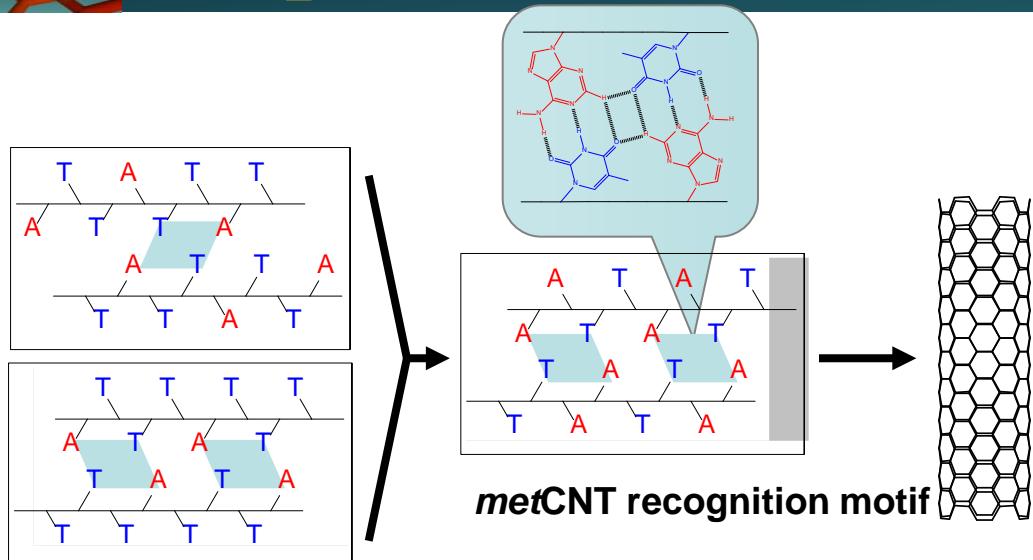


c

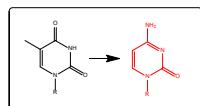


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# Sequence motif variation



## **semiCNT recognition motifs**



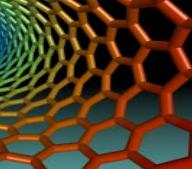
# Enabled single chirality armchair nanotubes

**TTATTATTATTATT** for (8,3)

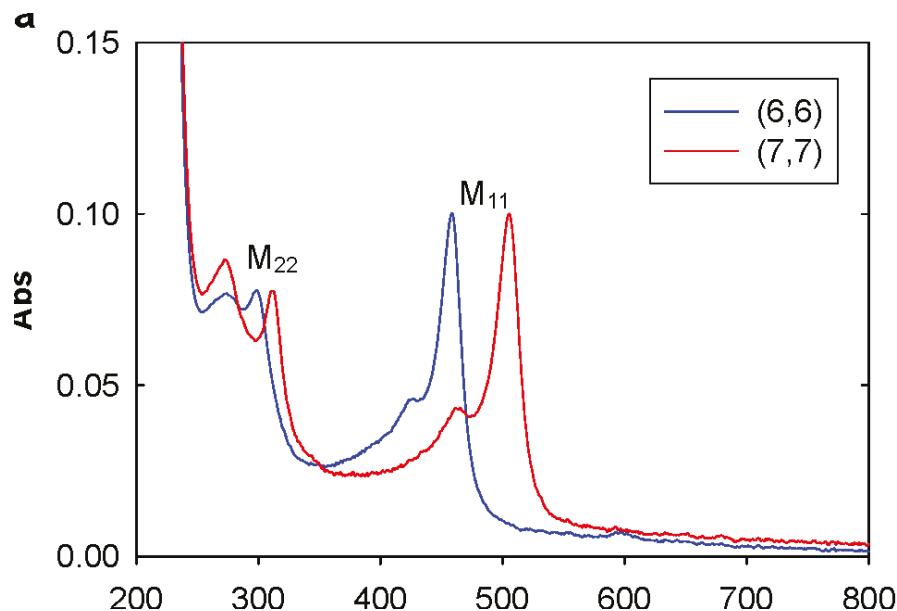
**C**TATTATTATTATT  
**TC**ATTATTATTATT  
TTA**C**TATTATTATT  
TTAT**C**ATTATTATT  
**TTATTACTATTATT** for (7,7)  
TTATTAT**C**ATTATT  
TTATTATTAC**T**ATT  
TTATTATTAT**C**ATT  
TTATTATTATTAC**T**  
TTATTATTATTAT**C**

# T to C scanning mutation

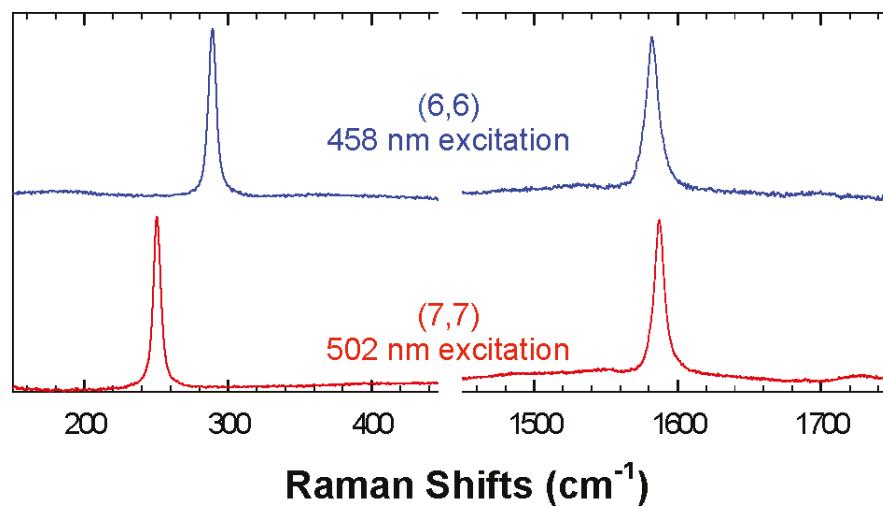
*J. Am. Chem. Soc.* 2011, 133, 129981

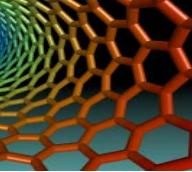


# Optical Properties of Armchair Tubes

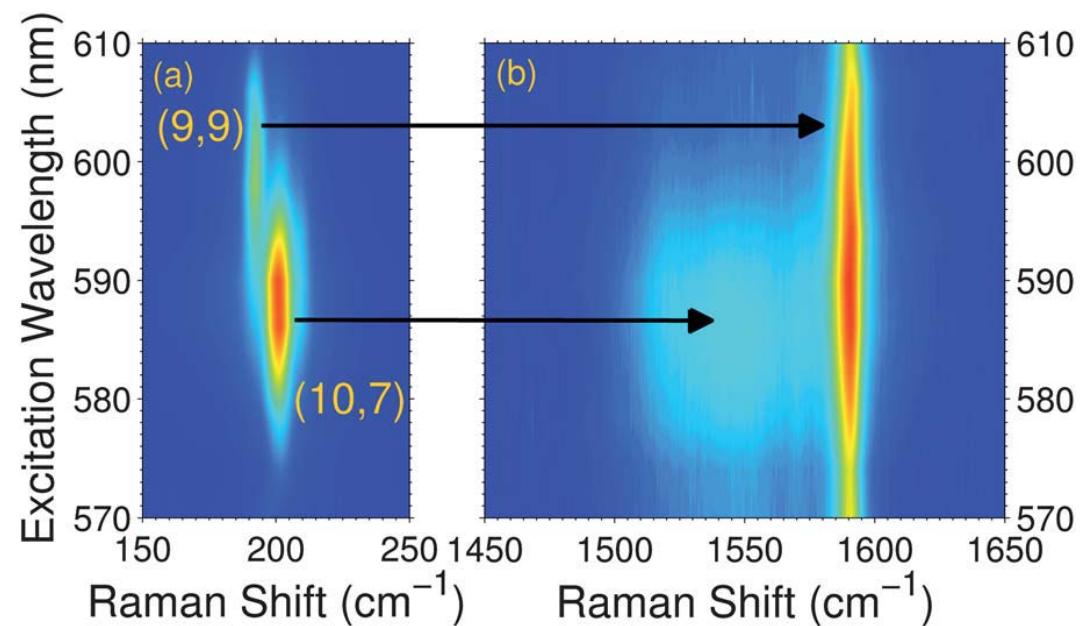
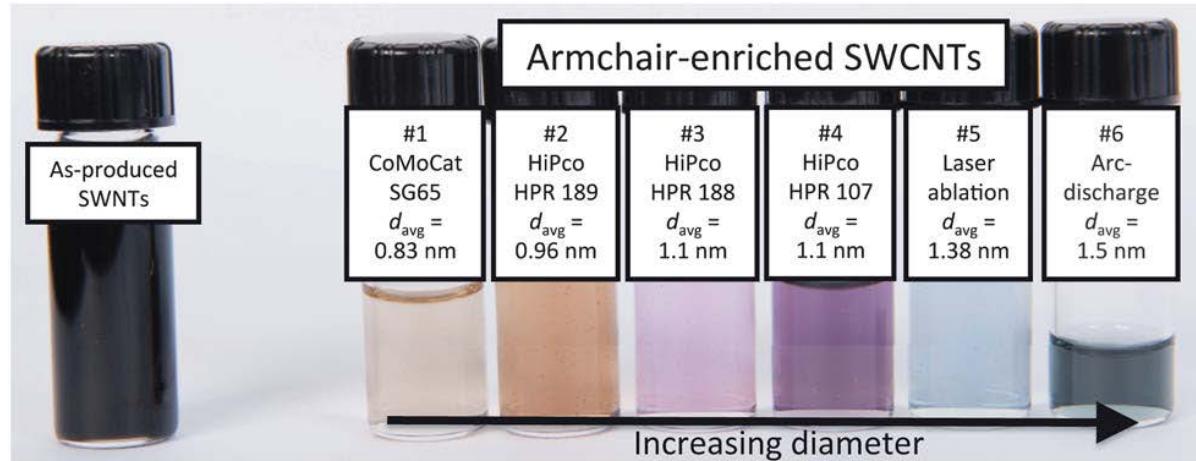


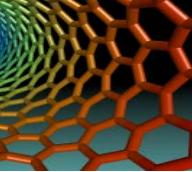
Single G band



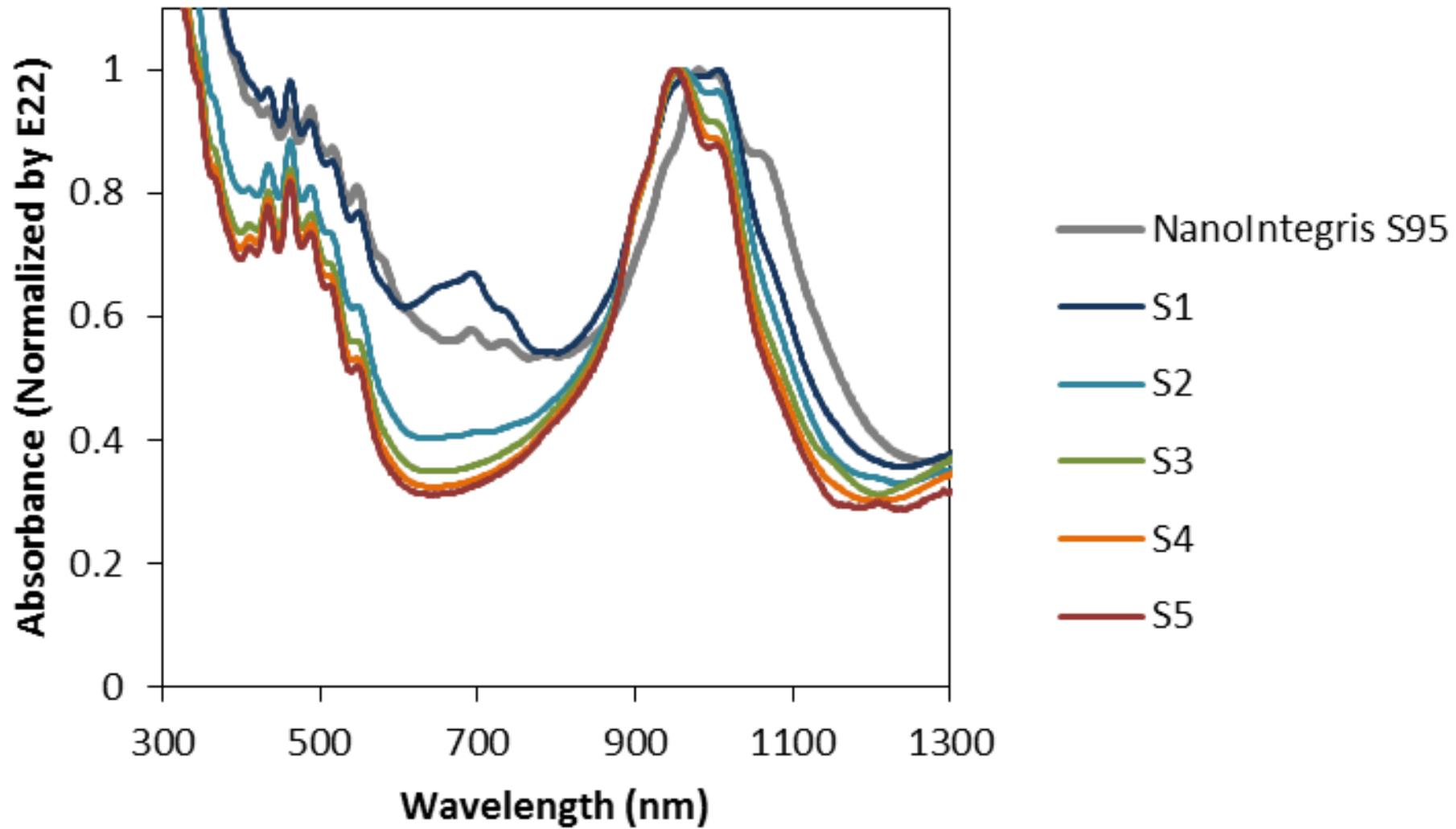


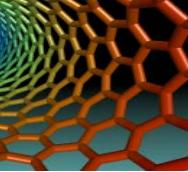
# Armchair Separation by Other Techniques



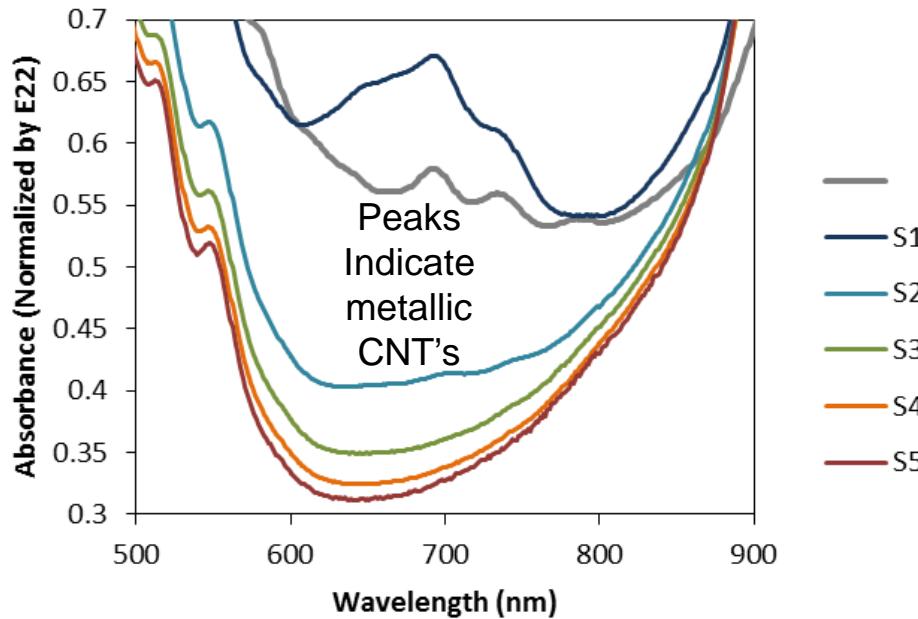


# Purity metrology for SWCNTs



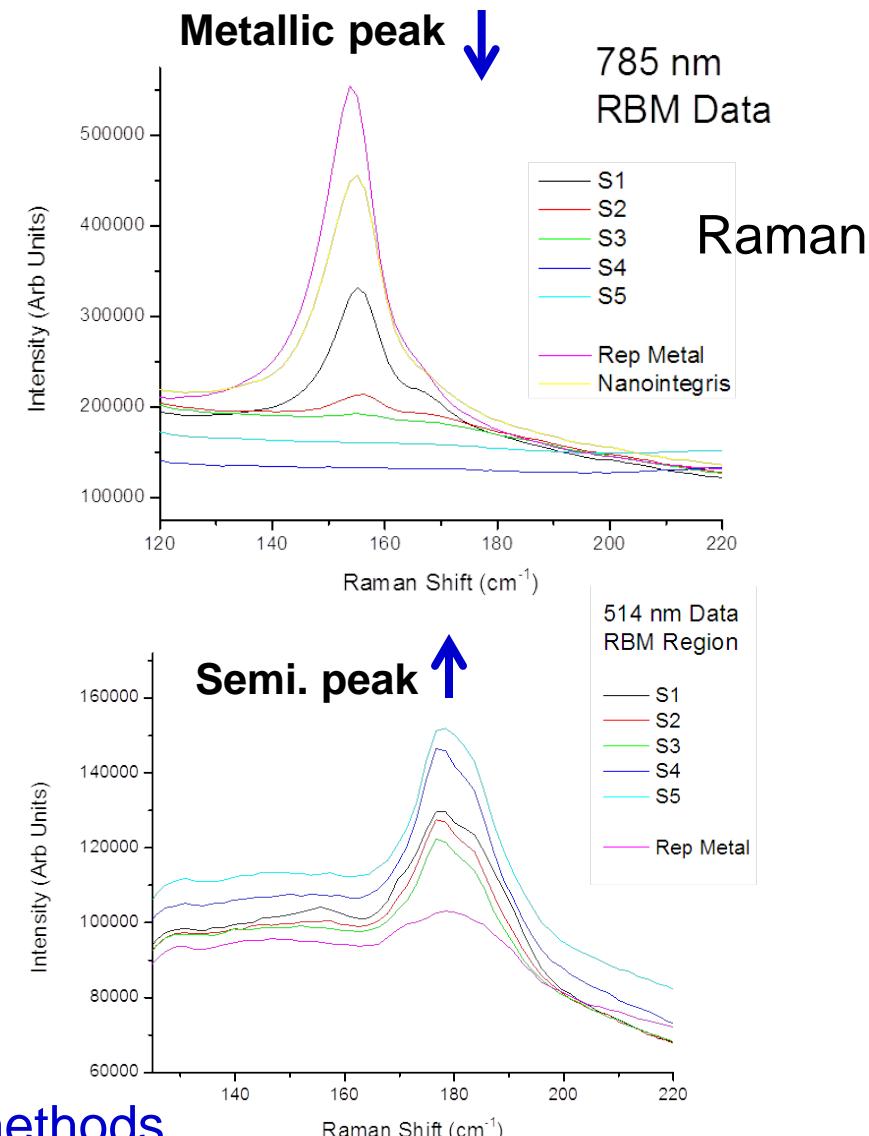


# Purity metrology for SWCNTs

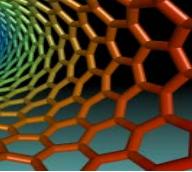


SWCNT's can now be purified to levels that test the resolution of purity metrology.

- Absorbance: quick
- Raman: more powerful, higher resolution
- Goal 99.999%



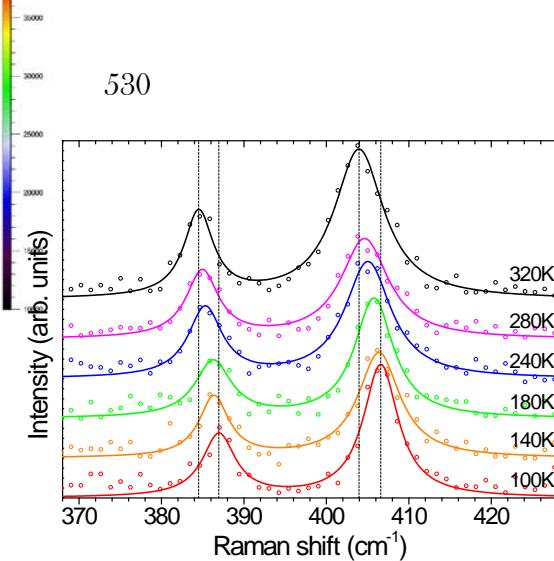
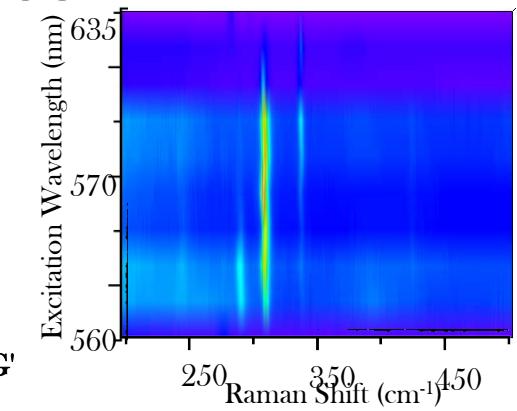
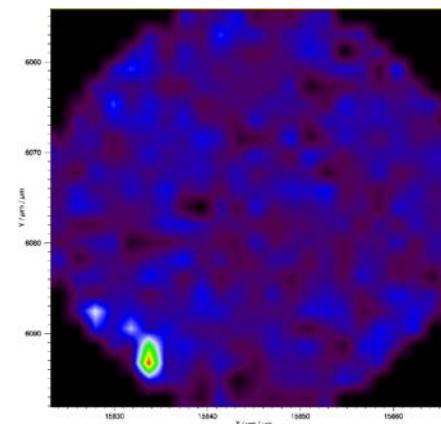
Actively improving accuracy of optical methods

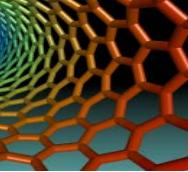


# Outline

*Raman spectroscopy applied to*

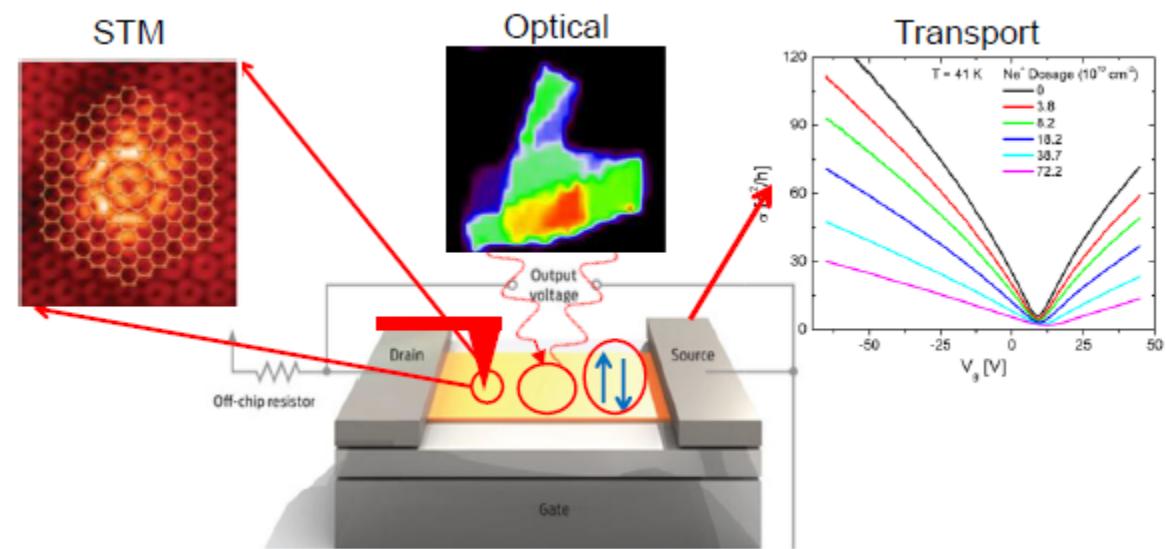
- Carbon Nanotubes
- 2D Materials
  - Graphene
  - $\text{MoS}_2$

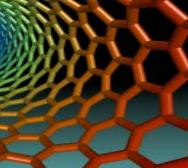




# NIST Graphene Team

## Bridging Measurement Length Scales to Advance Graphene Device Technologies





# Twisted Graphene

NANO  
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[pubs.acs.org/NanoLett](https://pubs.acs.org/NanoLett)

## Angle-Resolved Raman Imaging of Interlayer Rotations and Interactions in Twisted Bilayer Graphene

Robin W. Havener,<sup>†</sup> Houlong Zhuang,<sup>‡</sup> Lola Brown,<sup>§</sup> Richard G. Hennig,<sup>‡</sup> and Jiwoong Park\*,<sup>§,¶,⊥</sup>

<sup>†</sup>School of Applied and Engineering Physics, Cornell University, Ithaca, New York 14853, United States

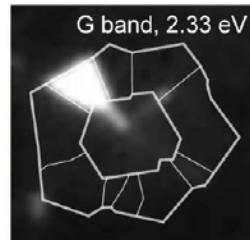
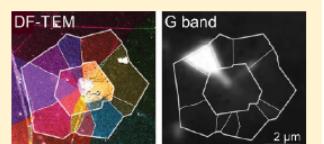
<sup>‡</sup>Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, United States

<sup>§</sup>Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, United States

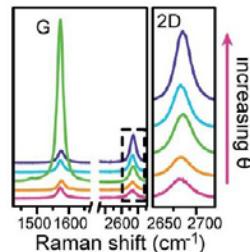
<sup>¶</sup>Kavli Institute at Cornell for Nanoscale Science, Cornell University, Ithaca, New York 14853, United States

Supporting Information

**ABSTRACT:** Few-layer graphene is a prototypical layered material, whose properties are determined by the relative orientations and interactions between layers. Exciting electrical and optical phenomena have been observed for the special case of Bernal-stacked few-layer graphene, but structure–property correlations in graphene which deviates from this structure are not well understood. Here, we combine two direct imaging techniques, dark-field transmission electron microscopy (DF-TEM) and widefield Raman imaging, to



Enhanced G



New Raman Modes

NANO  
LETTERS

Letter

[pubs.acs.org/NanoLett](https://pubs.acs.org/NanoLett)

## Observation of Layer-Breathing Mode Vibrations in Few-Layer Graphene through Combination Raman Scattering

Chun Hung Lui,<sup>†</sup> Leandro M. Malard,<sup>†</sup> SukHyun Kim,<sup>†</sup> Gabriel Lantz,<sup>†</sup> François E. Laverge,<sup>†</sup> Riichiro Saito,<sup>‡</sup> and Tony F. Heinz<sup>\*†</sup>

<sup>†</sup>Departments of Physics and Electrical Engineering, Columbia University, 538 West 120th Street, New York, New York 10027, United States

Nano Research  
DOI 10.1007/s12274-013-0304-z

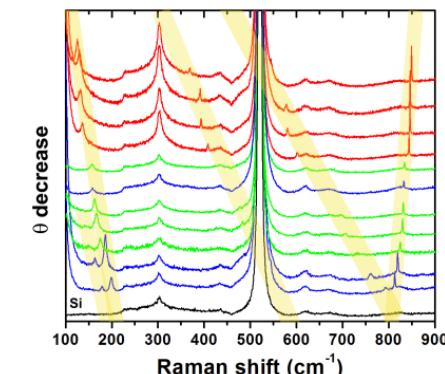
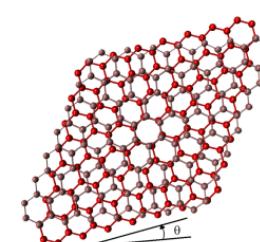
Research Article

ISSN 1998-0124

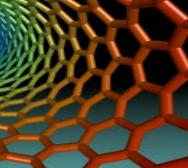
CN 11-5974/O4

## Raman-scattering study of the phonon dispersion in twisted bi-layer graphene

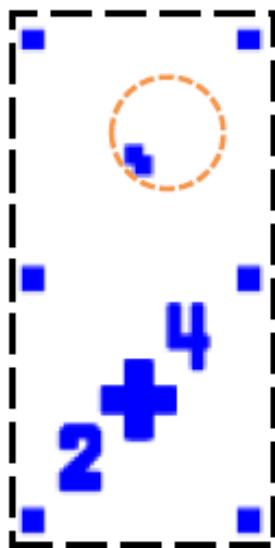
Jessica Campos-Delgado<sup>1</sup> (✉), Luiz G. Cançado<sup>2</sup>, Carlos A. Achete<sup>3</sup>, Ado Jorio<sup>2</sup>, Jean-Pierre Raskin<sup>1</sup>



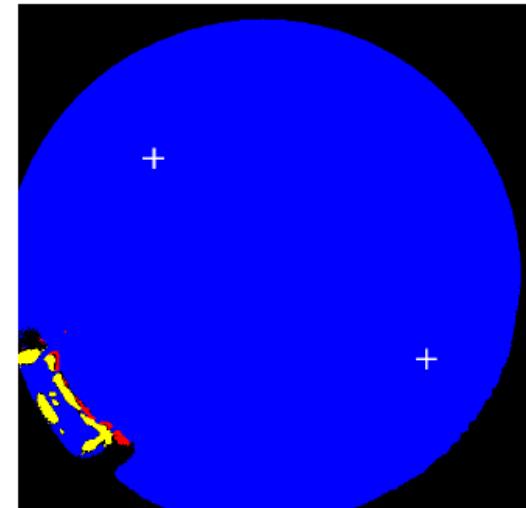
NIST



# Correlating LEEM with Raman

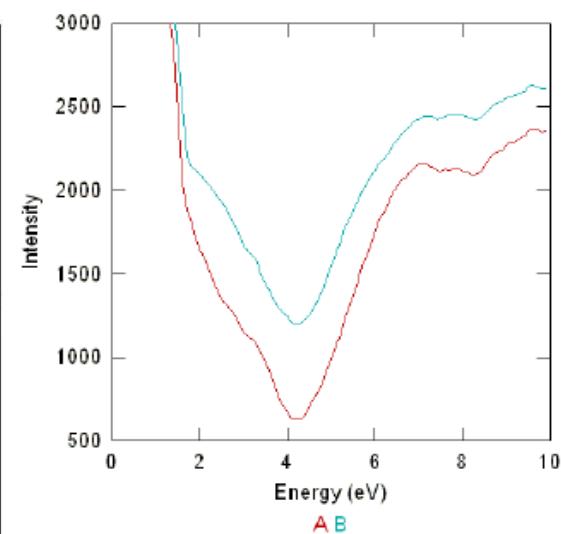
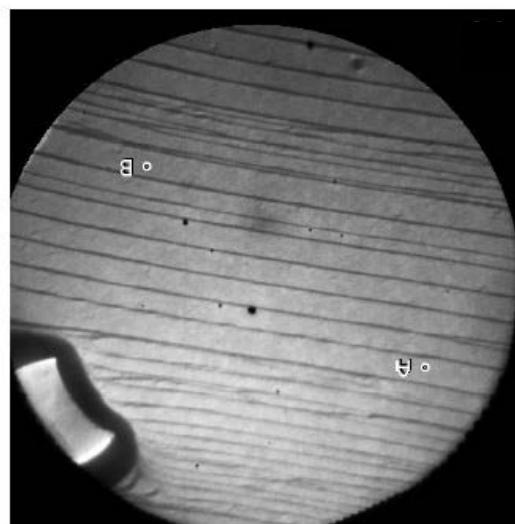


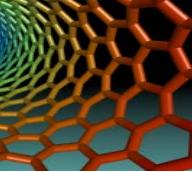
**Thickness Map  
Uniformly Single Layer**



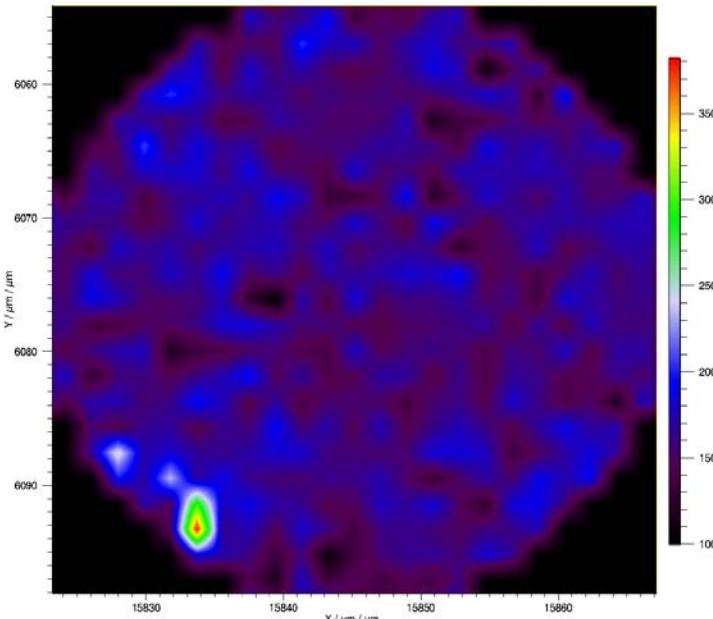
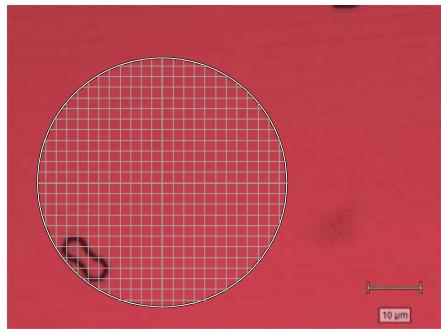
**Reflectivity Image  
@ 5.7 eV**

Two respective curves

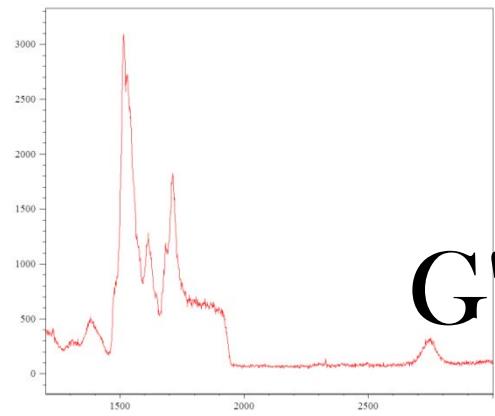




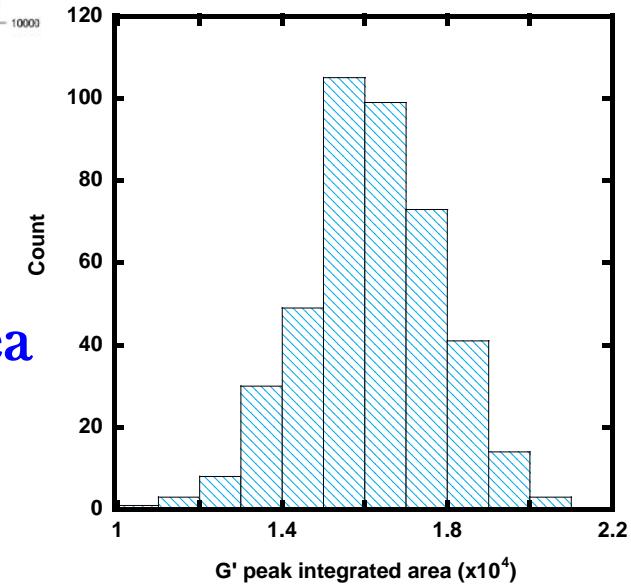
# Correlating LEEM with Raman

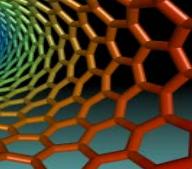


**G' peak  
Integrated area  
map**



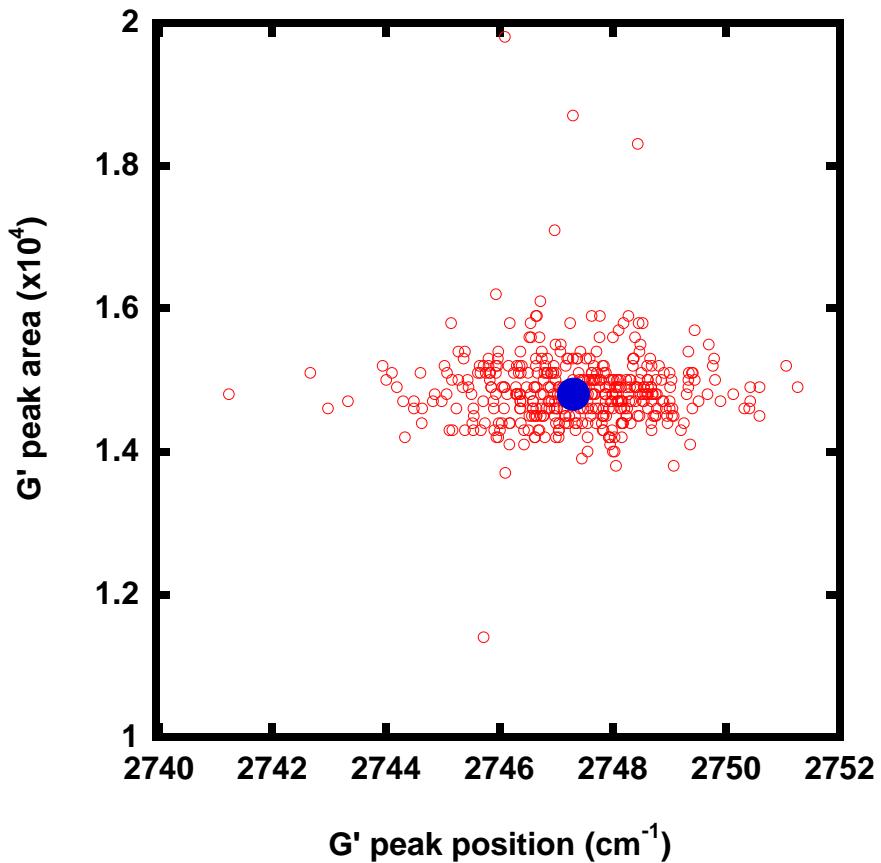
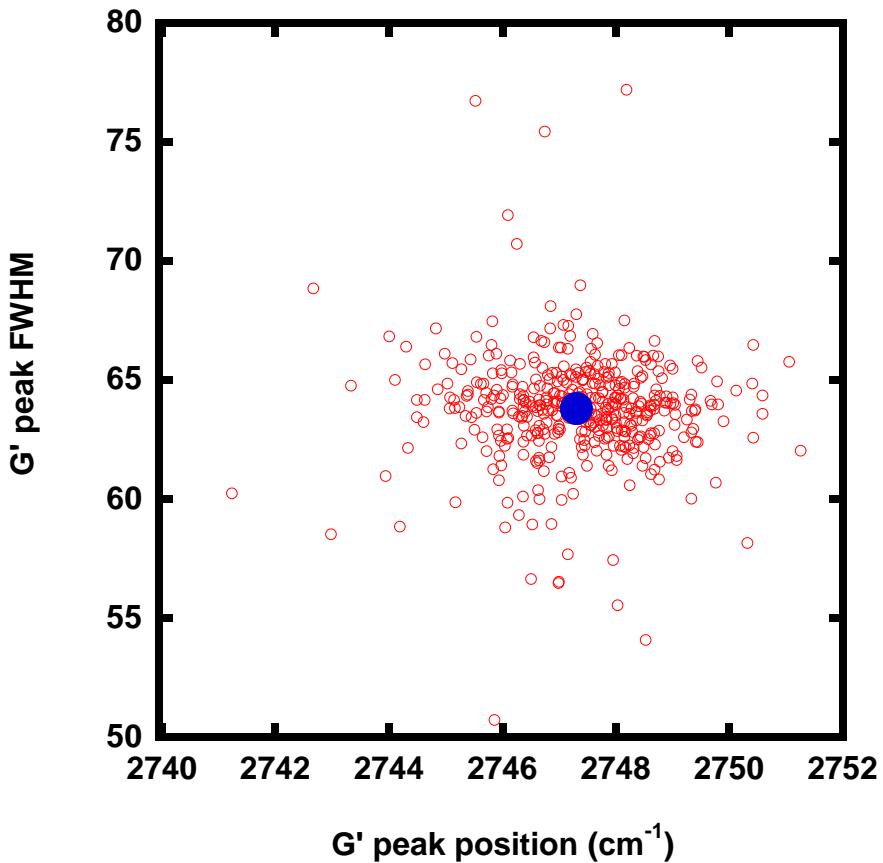
**2 micron steps  
Average  
Integrated Area  
 $1.61 \pm 0.19$**

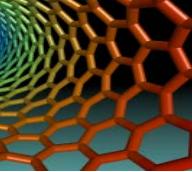




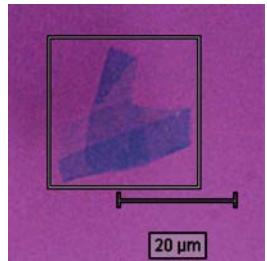
# Variation in Raman Data for Single Layer

Blue dots are average value

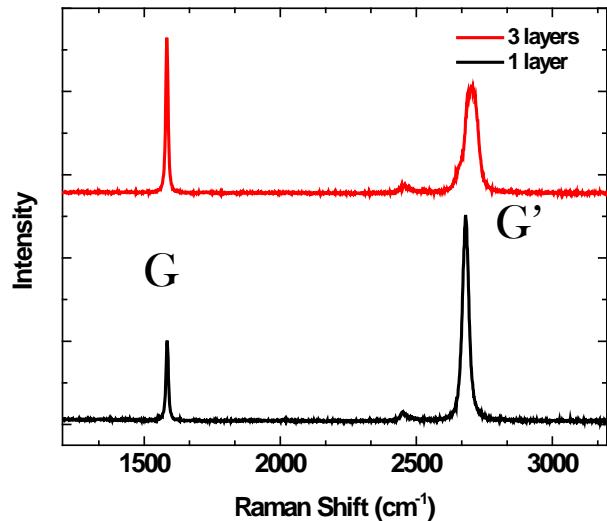




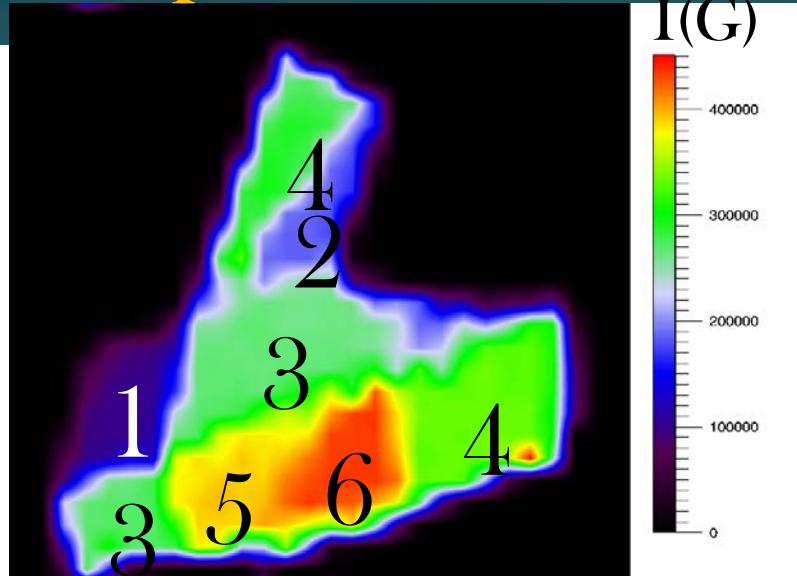
# Raman Mapping on Graphene



Optical image



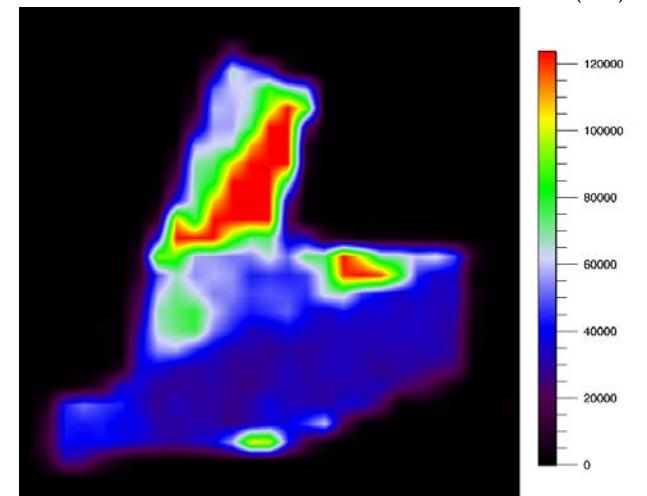
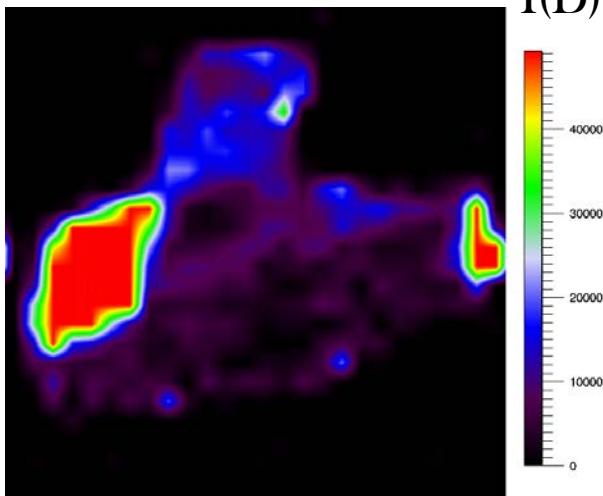
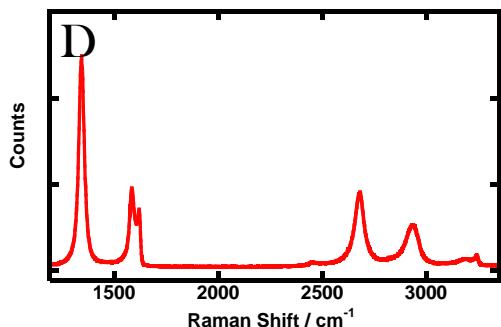
Raman Spectra

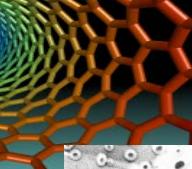


Raman mapping

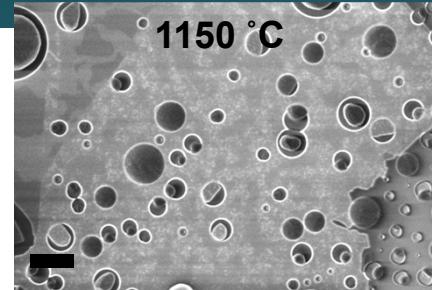
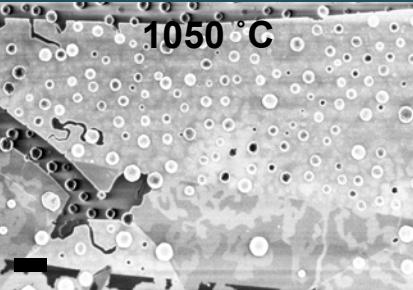
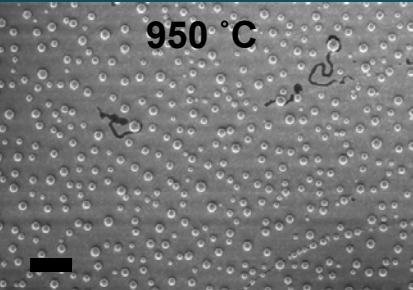
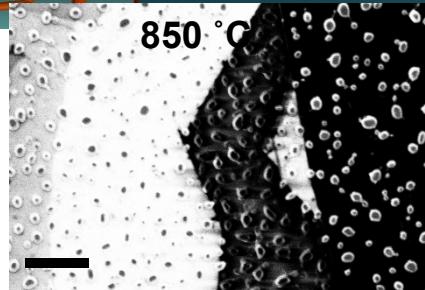
## Tracking chemical transformation of graphene

D peak shows up due to chemical reaction on graphene

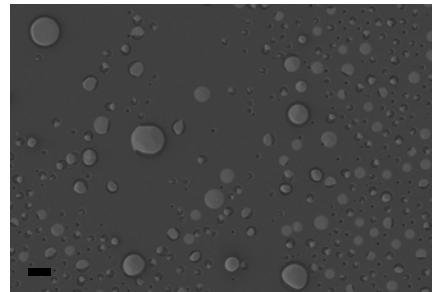
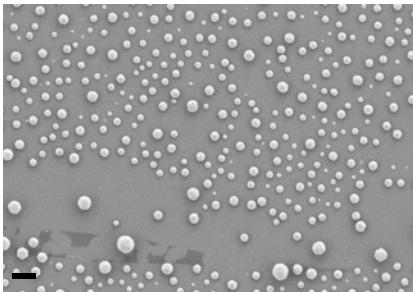
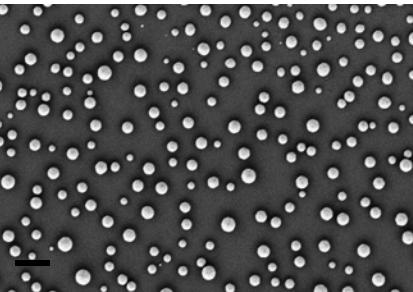
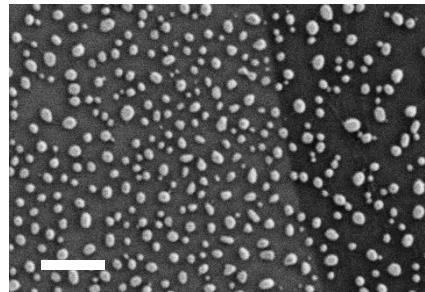




# Etching Graphene by Metallic Nanoparticles



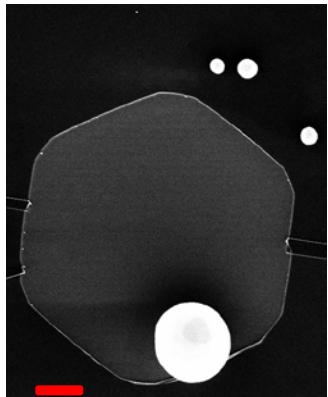
InLens detector



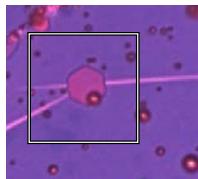
SE2 detector

scale bar: 1  $\mu$ m

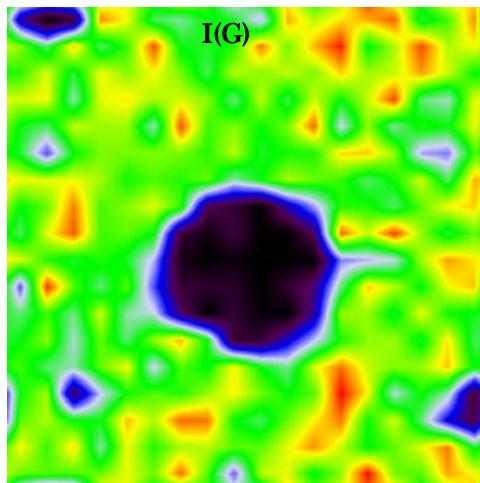
SEM



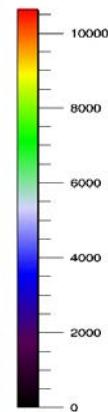
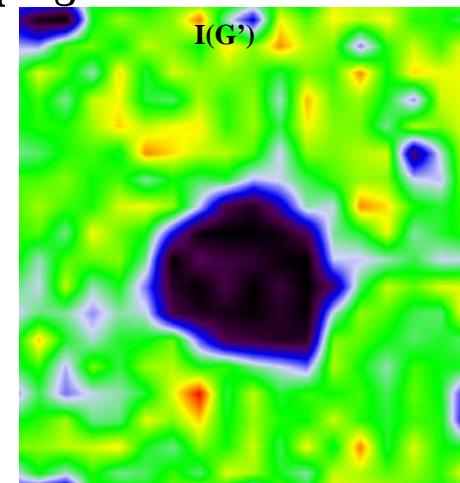
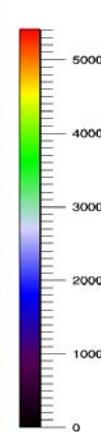
Hexagon  
Pits  
Zigzag Edge

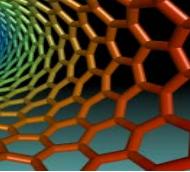


Scale bar: 1  $\mu$ m



Raman Mapping





# Cutting Graphene with Cu Nanoparticles

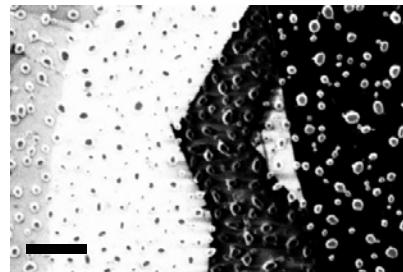
*Summary of Cu Annealing*

850 °C

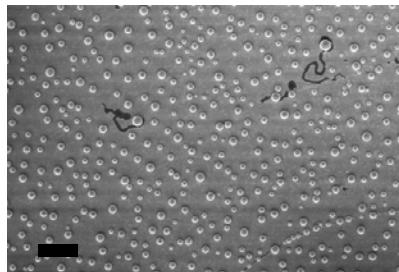
950 °C

1050 °C

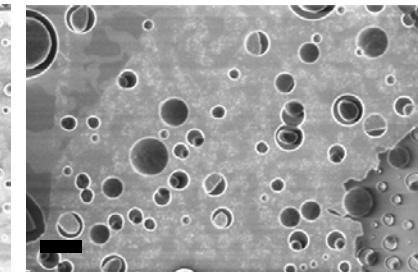
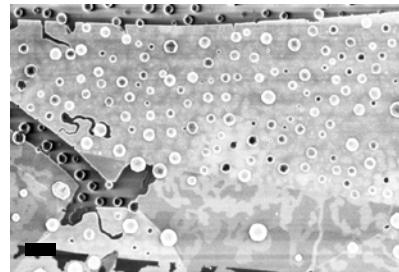
1150 °C



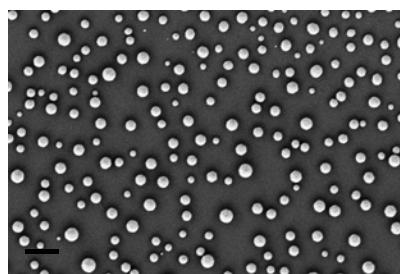
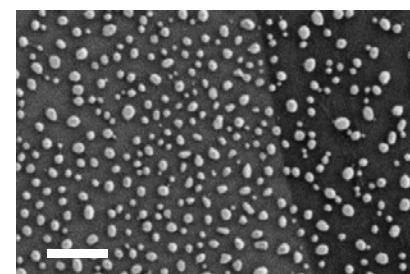
monolayer



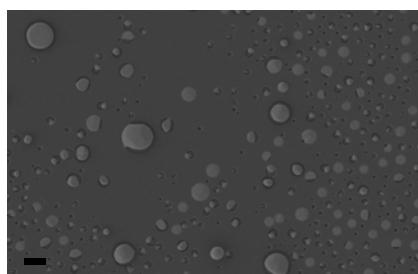
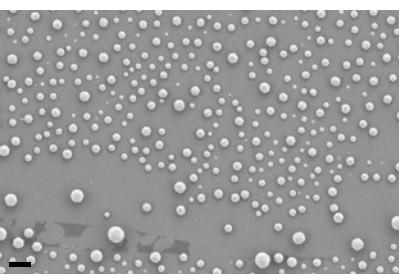
InLens



monolayer



SE2

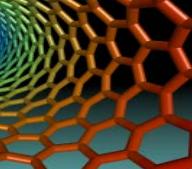


graphite

scale bar: 1 μm

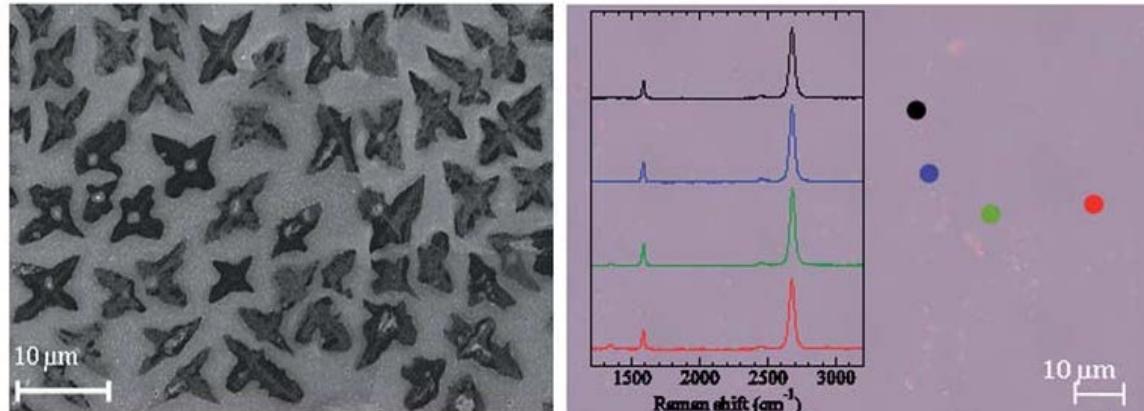
*Selected as a talk for Graphene Week 2011, Austria*

NIST

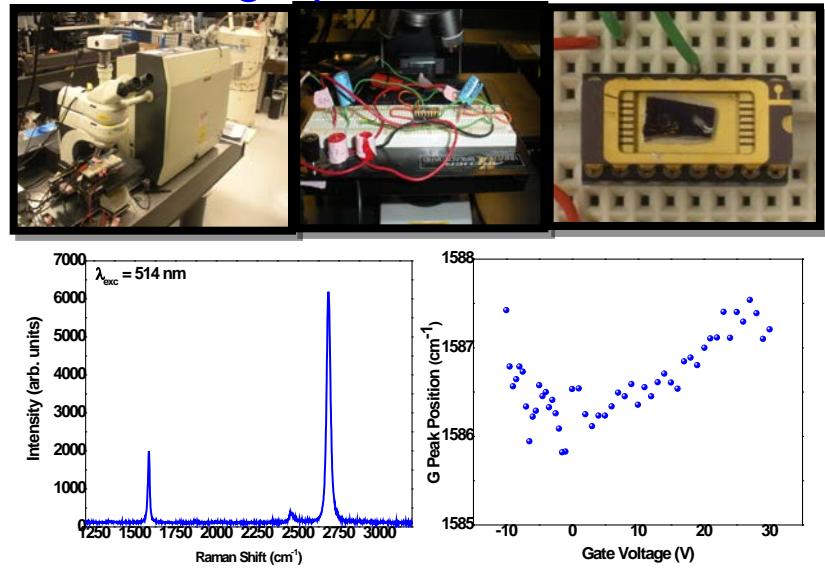


# Raman Spectroscopy of Graphene

## Liquid Carbon Source CVD graphene

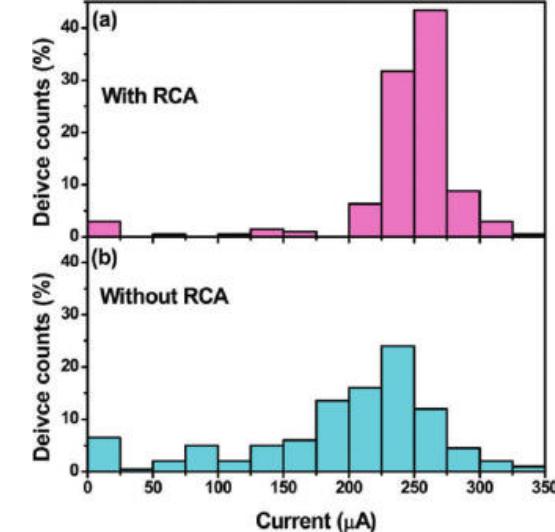


## Gated graphene transistors

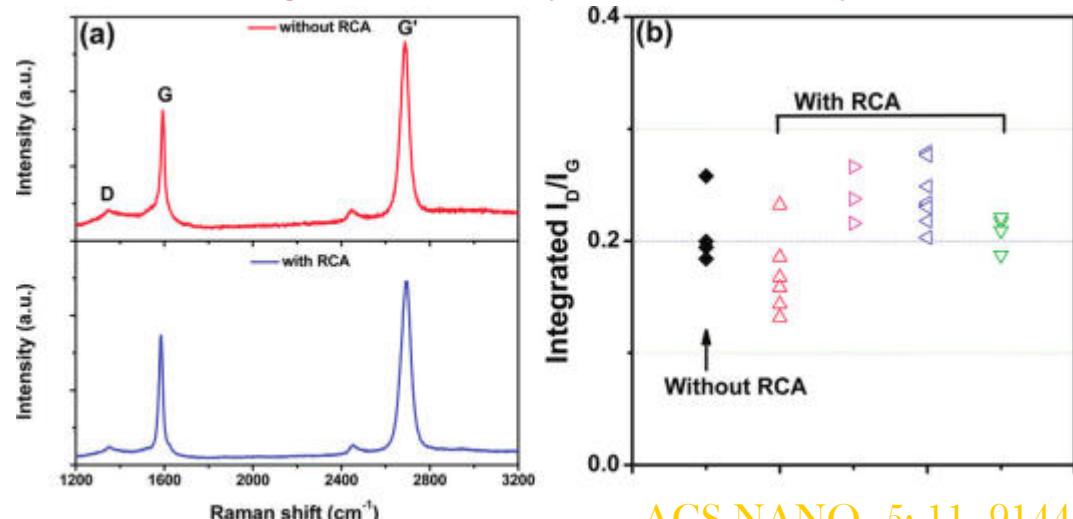


Monitors doping level in graphene devices

## CVD graphene Transfer



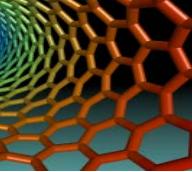
RCA cleaning doesn't noticeably affect defect density.



ACS NANO 5: 11 9144

J. Mater. Chem., 2011, 21, 16057

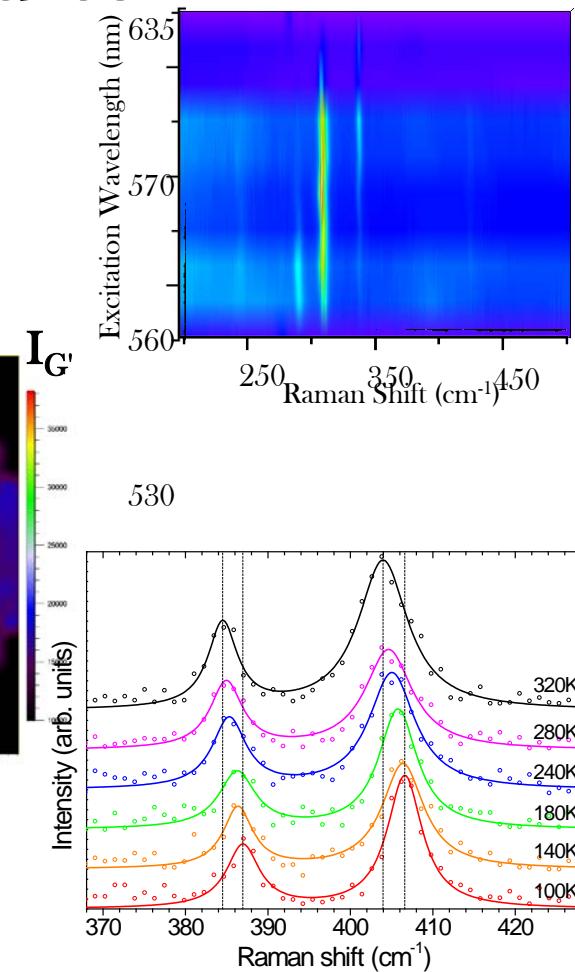
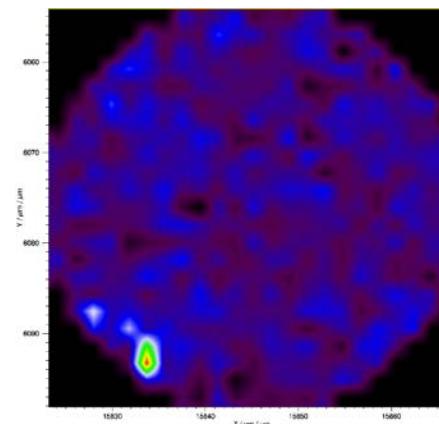
NIST

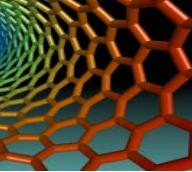


# Outline

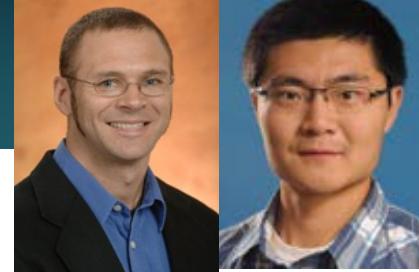
*Raman spectroscopy applied to*

- Carbon Nanotubes
- 2D Materials
  - Graphene
  - $\text{MoS}_2$





# Introduction & Motivation



- Graphene stimulates interest in related layered materials, e.g., MoS<sub>2</sub>:  
single layer, **direct band gap** ~1.9eV  
mobility m < graphene

applications: transistors, photovoltaics, valleytronics

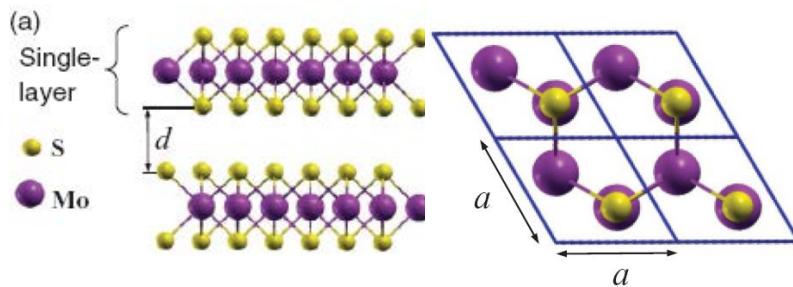
- MoS<sub>2</sub> structure: layered trigonal prismatic,

1L non-centrosymmetric P6m2 (D<sub>3h</sub>)

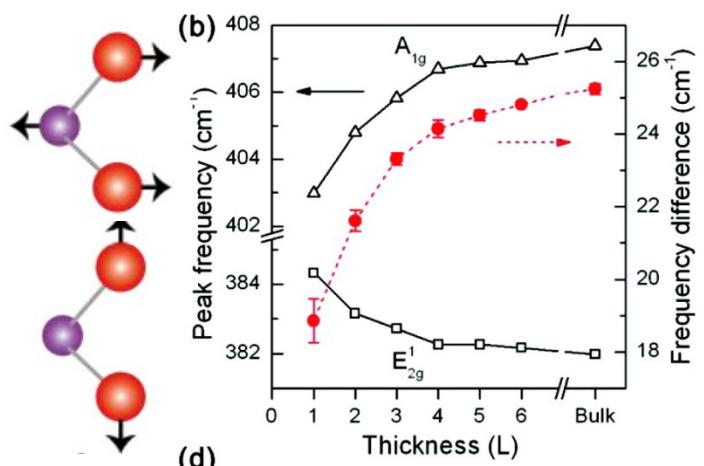
- Raman spectroscopic characterization of MoS<sub>2</sub>

- two prominent Raman-active phonons symmetry  
E<sub>2g</sub><sup>1</sup> (in-plane) & A<sub>1g</sub> (out-of-plane)
- quantifies layer#: peak difference

- Understanding of optical & thermal properties important for device applications

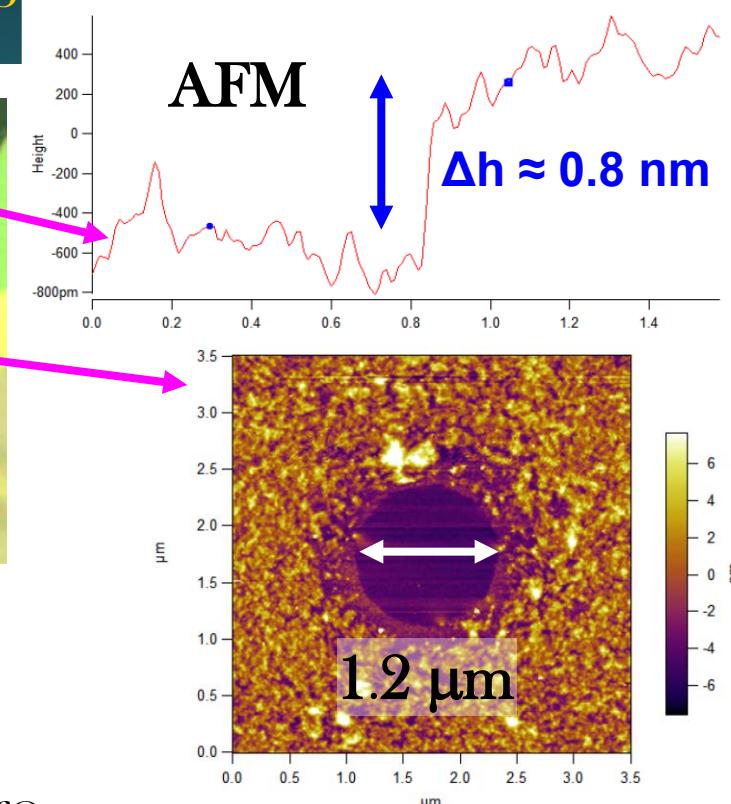
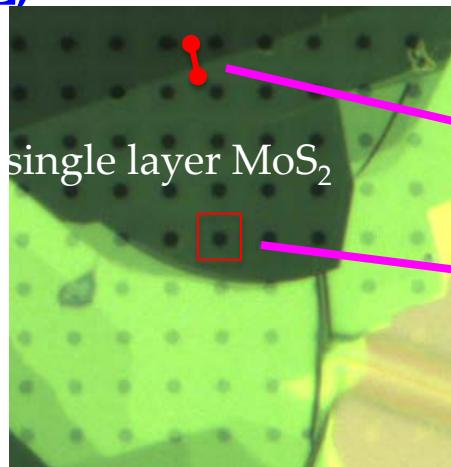
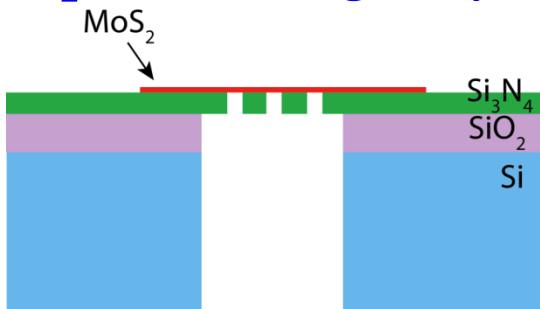


Molina-Sanchez *et al.*, PRB **84**, 155413 (2011)



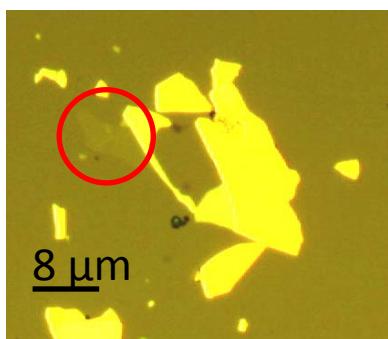
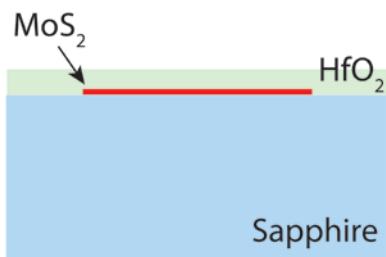
# MoS<sub>2</sub> Monolayer Samples

Suspended single layer (1L)

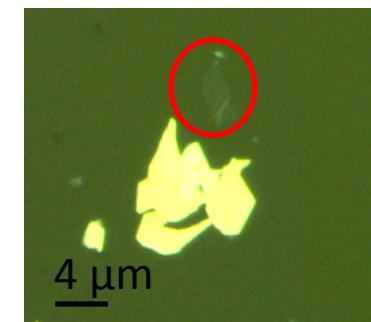
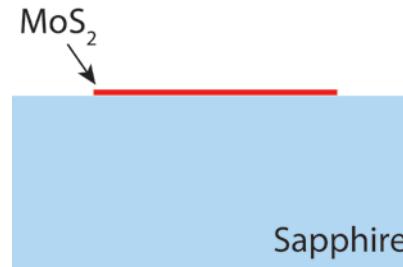


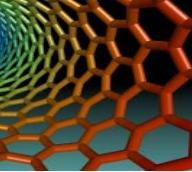
Substrate (Al<sub>2</sub>O<sub>3</sub>) supported

with HfO<sub>2</sub> overcoat

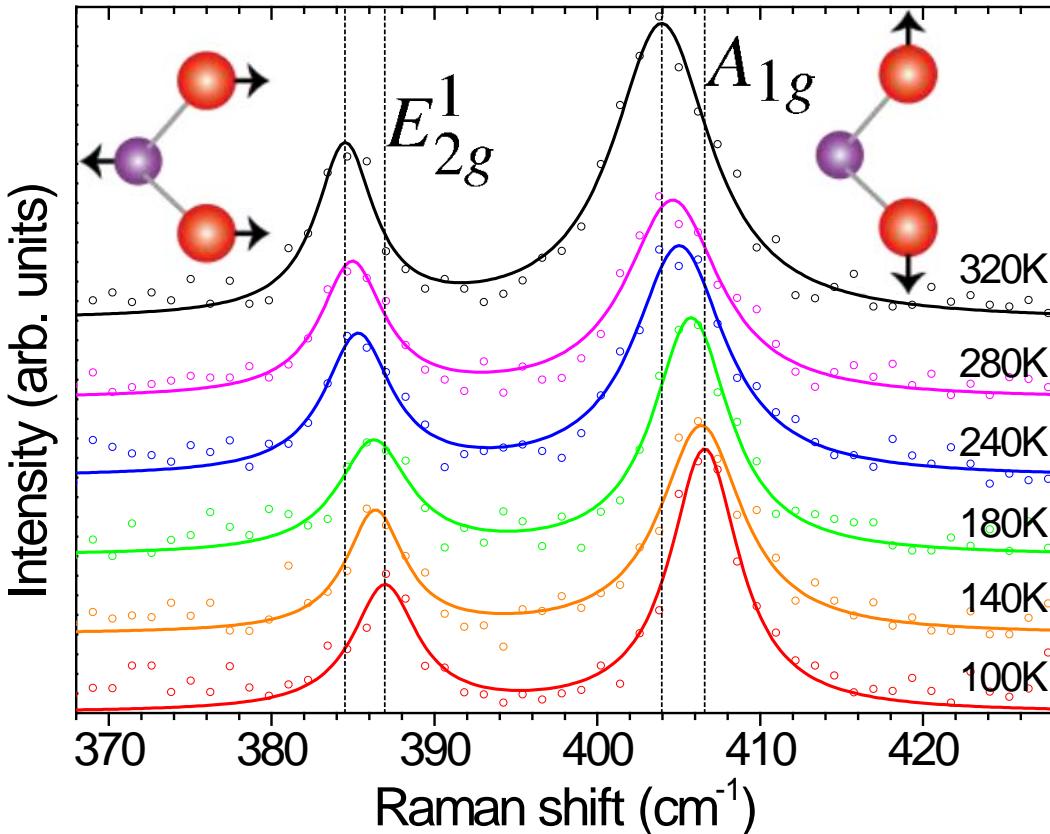


w/o HfO<sub>2</sub> overcoat





# Temperature-Dependent Raman Spectra

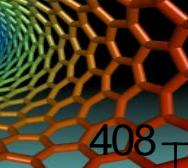


$\lambda_{\text{ex}} = 514.5 \text{ nm}$

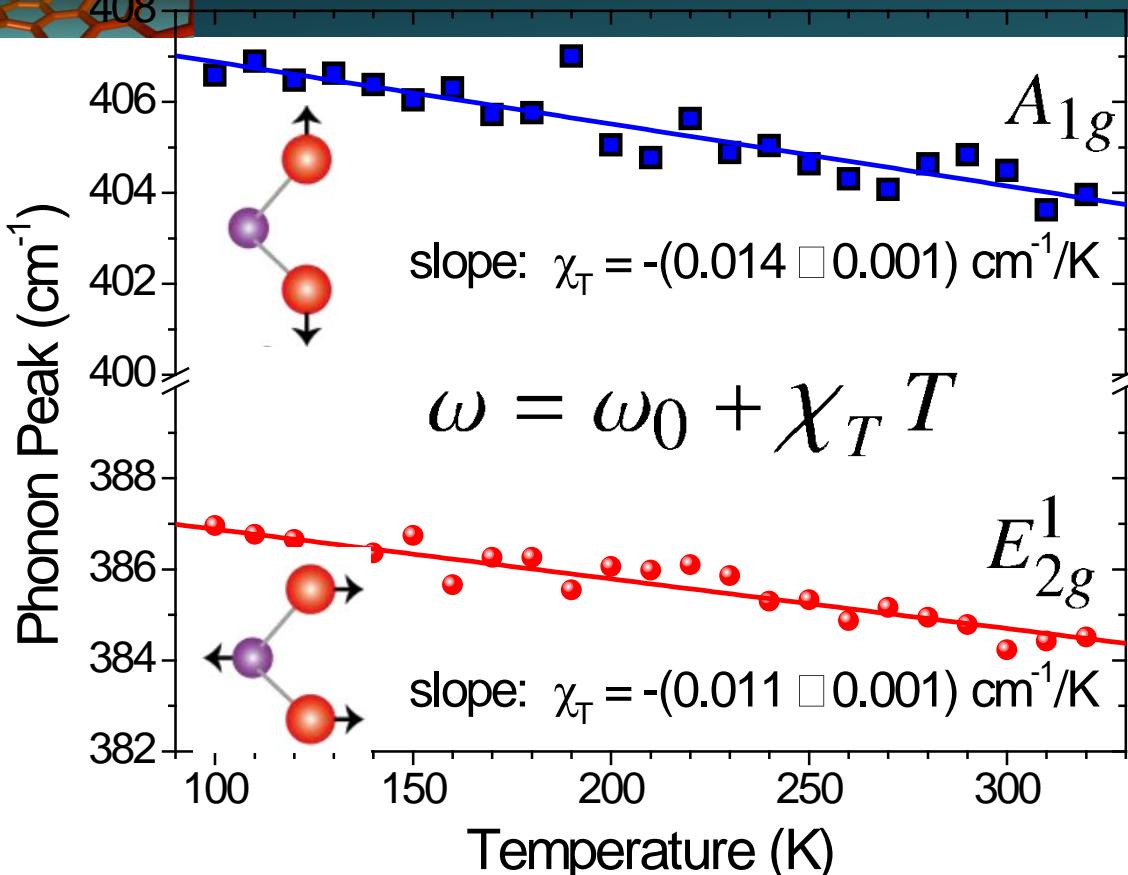
< 0.2 mW (50X NA 0.55)

~ 1.2  $\mu\text{m}$  diffraction-limited spot

- observe two prominent Raman-active phonons:  $E_{2g}^1$  (in-plane) and  $A_{1g}$  (out-of-plane)
- phonons soften with increasing temperature
- low optical power (intensity) to minimize thermal effects, *e.g.*, avoid local heating & sample damage



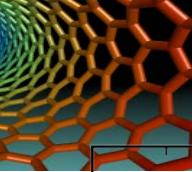
# Temperature-Dependent Phonon Peaks



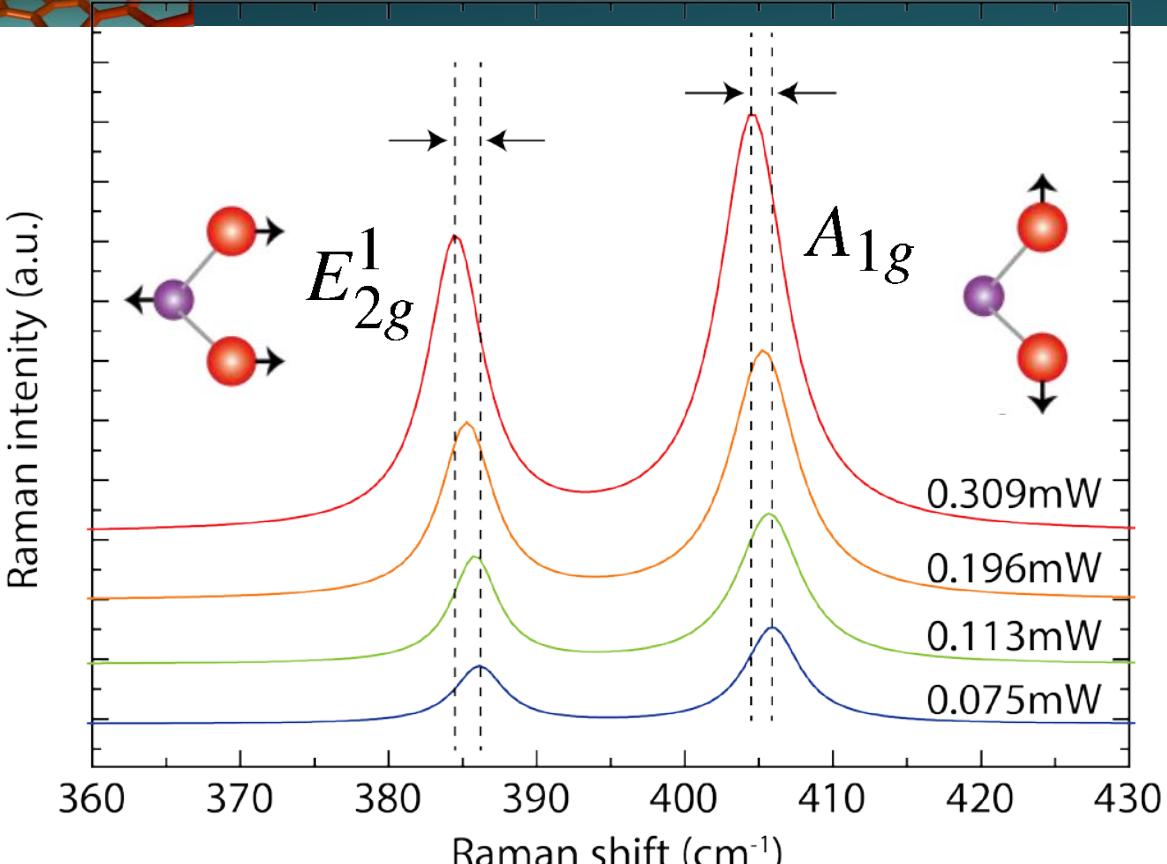
$\text{MoS}_2$	$\chi_T (\text{cm}^{-1}/\text{mW})$
$E_{2g}^1$	$A_{1g}$
1L suspended	-0.011
	-0.014
$\text{Graphene}$	$\chi_T (\text{cm}^{-1}/\text{mW})$
$G\text{-band } E_{2g}$	
1L suspended <sup>1</sup>	-0.016

<sup>1</sup> Balandin *et al.*, *NL* **8**, 902 (2008)

- Phonon frequencies **soften linearly with increasing temperature**
- Anharmonic lattice potential → phonon scattering, thermal expansion
- Extract linear temperature coefficient  $\chi_T$  ( $\text{cm}^{-1}/\text{K}$ )
- $A_{1g}$  slightly more sensitive to temperature change



# Laser Power-Dependent Raman Spectra



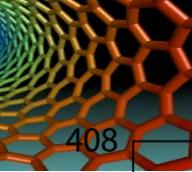
room temperature

$\lambda_{\text{ex}} = 488 \text{ nm}$

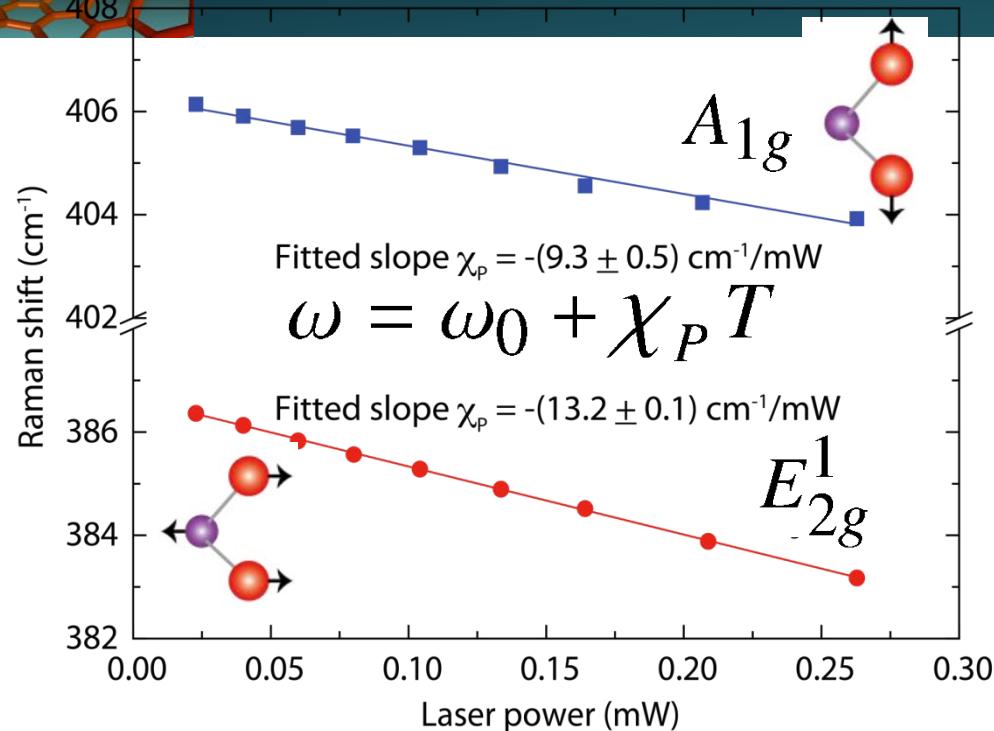
100X NA 0.95

~ 0.7  $\mu\text{m}$  diffraction-limited spot

- Room temperature measurement
- local heating **softens** phonon peak frequency
- sample damage for power > 2mW



# Laser Power-Induced Phonon Peak Shifts



<b>MoS<sub>2</sub></b>	$\chi_p (\text{cm}^{-1}/\text{mW})$	
	$E_{2g}^1$	$A_{1g}$
<b>1L suspended</b>	-13.2	-9.3
1L supported <sup>1</sup>	-0.09	-0.40

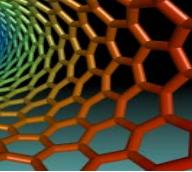
[1] R. Yan *et al.*, arXiv:1211.4136

<b>Graphene</b>	$\chi_p (\text{cm}^{-1}/\text{mW})$
1L suspended <sup>2</sup>	-1.3
1L supported <sup>3</sup>	-0.7

<sup>2</sup> Balandin *et al.*, Nano. Lett. **8**, 902 (2008)

<sup>3</sup> Lee *et al.*, PRB **83**, 081419 (2011)

- Linear at low power, saturates above 0.3 mW (not shown)
- $A_{1g}$  less sensitive to power
- substrate serves as heat sink
- 10x larger  $\chi_p$  coefficient than graphene



# Optical Absorption in Monolayer MoS<sub>2</sub>

Thermal conductivity  $\kappa = \frac{A}{2\pi t} \frac{\partial P}{\partial T}$

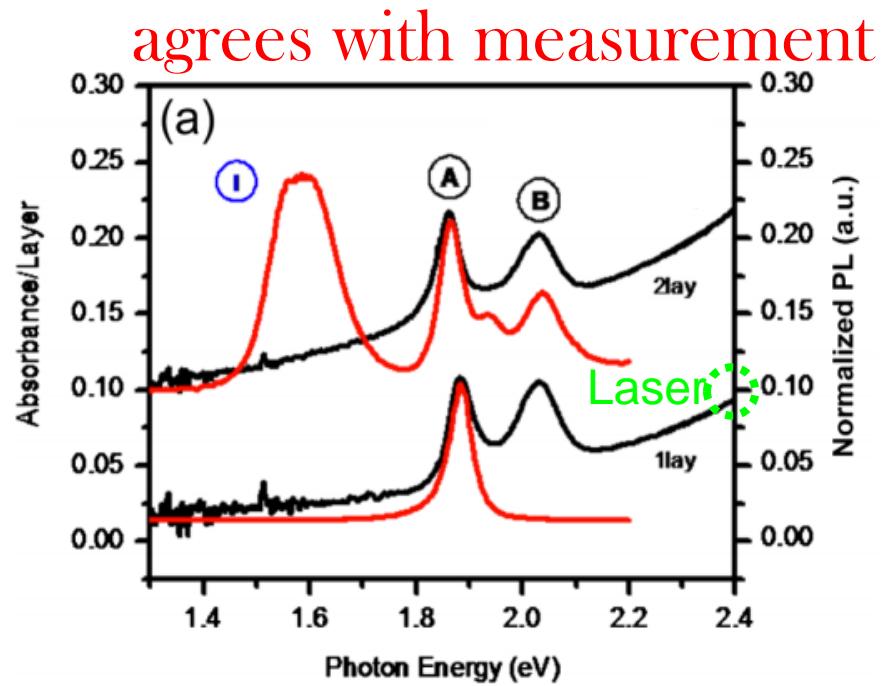
$$\begin{array}{l} n_0 = 1 \\ \text{suspended MoS}_2 \\ \\ n_1 = 1 - 5i \\ \\ n_2 = 1 \end{array}$$

Model suspended 1L with complex index of refraction  $n_1 = 5 - i$  surrounded by air obtain transmittance  $T$  & reflectance  $R$

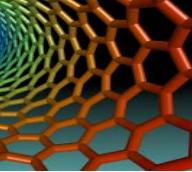
$$\begin{aligned} T &= \left| \frac{t_{01}t_{12} e^{i\phi_1}}{1 - r_{10}^2 e^{2i\phi_1}} \right|^2 & t_{01} &= \frac{E_t}{E_i} \\ R &= \left| \frac{r_{01}(1 - e^{i2\phi_1})}{1 - r_{10}^2 e^{i2\phi_1}} \right|^2 & r_{01} &= \frac{E_r}{E_i} \\ && \phi_1 &= 2\pi \tilde{n}_1 v d_1 \end{aligned}$$

absorbance:  $A = 1 - (R + T) = 0.09$   
use this for determining incident laser power absorbed by sample

Beal & Hughes, JPC: Sol State Phys (1979)



Mak *et al.*, PRL 105, 136805 (2010)



# Estimating Thermal Conductivity

Thermal conductivity

$$\kappa = \frac{A}{2\pi t} \frac{\partial P}{\partial T}$$

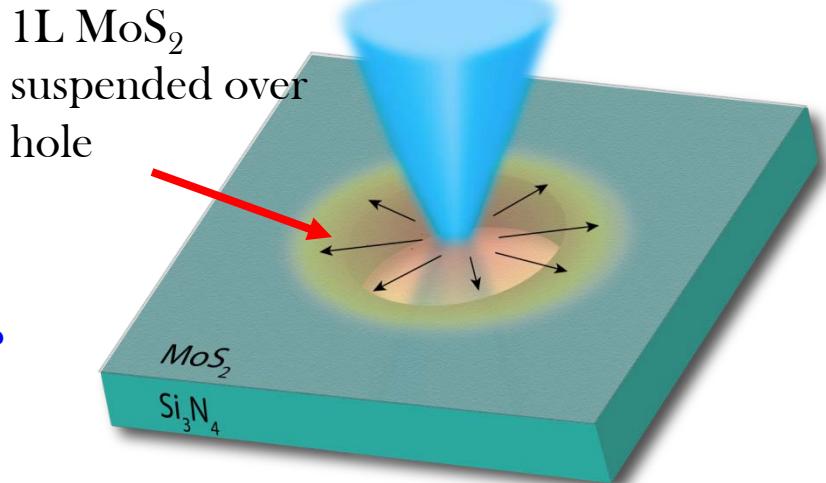
Rewrite  $\kappa$  in terms of phonon shifts linear temperature & power coefficients,  $\chi_T$  &  $\chi_P$

$$\kappa = \frac{A}{2\pi t} \frac{\partial P}{\partial \omega} \frac{\partial \omega}{\partial T} = \frac{A}{2\pi t} \frac{\left(\frac{\partial \omega}{\partial T}\right)}{\left(\frac{\partial \omega}{\partial P}\right)}$$

$$\boxed{\kappa = \frac{A}{2\pi t} \frac{\chi_T}{\chi_P}}$$

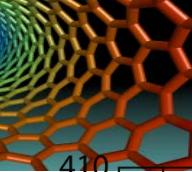
thermal conductivity  $\kappa$   
from measured  $\chi$  values

\*  $A_{1g}$  dominates  $K$  in MoS<sub>2</sub>

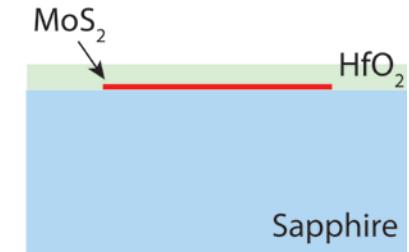
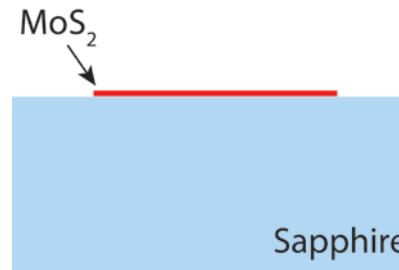
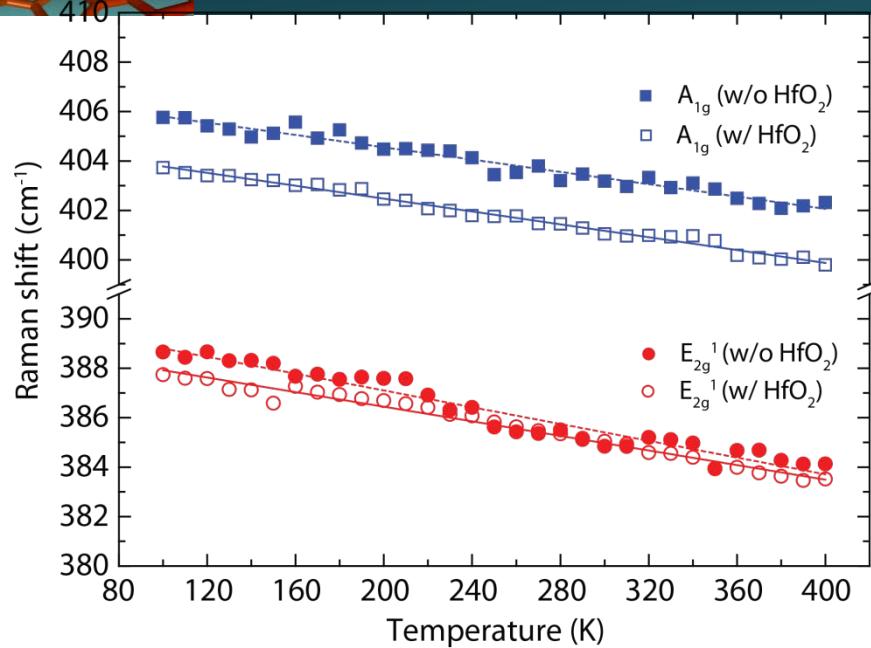


Suspended single layer	$\kappa$ W/(m K)
MoS <sub>2</sub>	27 +/- 20% *
graphene <sup>1</sup>	5000

<sup>1</sup> Balandin *et al.*, Nano Lett. **8**, 902 (2008).



# Substrate-Supported 1L MoS<sub>2</sub>



- $\text{Al}_2\text{O}_3$  &  $\text{HfO}_2$  similar thermal expansion & larger than bulk MoS<sub>2</sub> → tensile strain  
Sapphire :  $7.3 \times 10^{-6}/\text{K}$ ,  $\text{HfO}_2$ :  $6.7 \times 10^{-6}/\text{K}$   
Bulk MoS<sub>2</sub> (in plane):  $4.9 \times 10^{-6}/\text{K}$
- $\text{HfO}_2$  induces  $A_{1g}$  shift → electronic doping<sup>1,2</sup>
- Consistent with theoretical prediction:  $A_{1g}$  more sensitive to el-ph coupling<sup>1</sup>

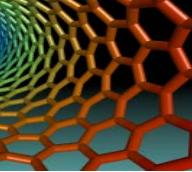
MoS <sub>2</sub>	$\chi_T$ (cm <sup>-1</sup> /mW)	
	$E_{2g}^1$	$A_{1g}$
w/ HfO <sub>2</sub>	-0.017	>-0.013
w/o HfO <sub>2</sub>	-0.015	>-0.013
suspended	-0.011	<-0.014

Thermal expansion: Sapphire : $7.3 \times 10^{-6}/\text{K}$

HfO<sub>2</sub>:  $6.7 \times 10^{-6}/\text{K}$

Bulk MoS<sub>2</sub> (in plan):  $4.9 \times 10^{-6}/\text{K}$

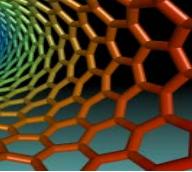
1. B. Chakraborty et al., PRB 85, 161403(R) (2012).
2. R. Yan et al., arXiv:1211.4136.



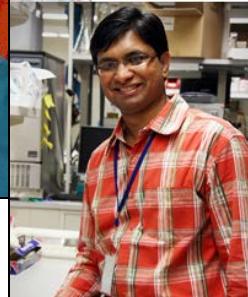
# Conclusions

Raman continues to be a novel  
characterization methods for  
nanoelectronics

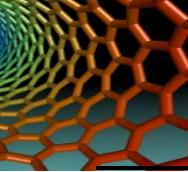
Thank you for your attention....



# Thanks the people who do the work



NIST

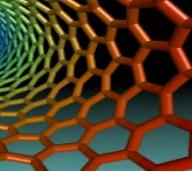


# Problem and Solution

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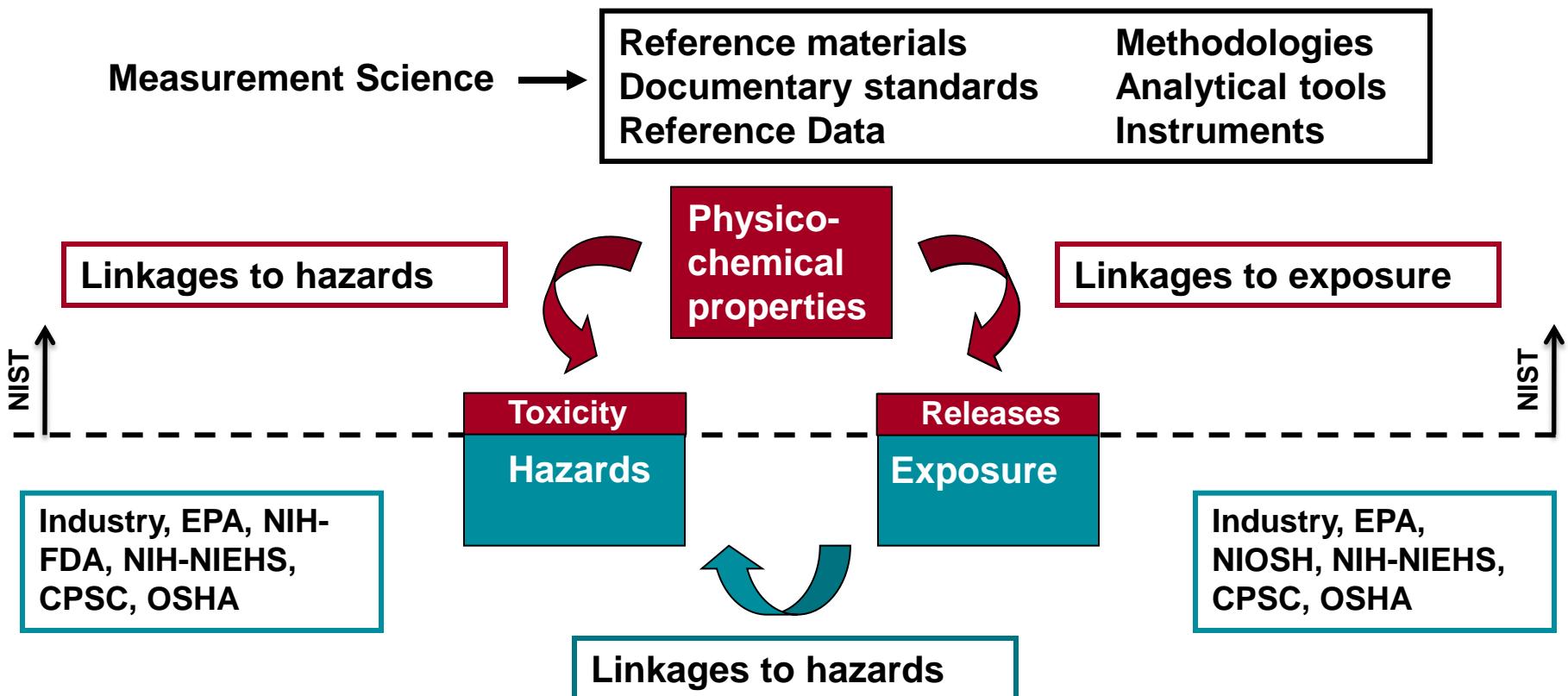
**Nanomaterials** and products that incorporate nanomaterials **pose *unknown risks*** throughout all stages of their life cycles, from initial sourcing through manufacture, use, disposal or recycling, and ultimate fate.

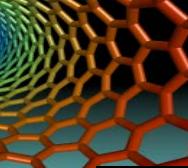
Sets of accurate data for physico-chemical properties, hazards, and exposure to enable science-based, lifecycle risk assessment and risk management of nanomaterials and products that incorporate them.



# NIST Role in the Solution

Create and disseminate critical measurement solutions for determining key *physico-chemical and toxicological properties of nanomaterials and release of nanomaterials* throughout the full life cycles of key nanomaterials and products containing these nanomaterials.





# Nano-EHS Technical Program

Measurement Science



Reference materials  
Documentary standards  
Reference Data

Methodologies  
Analytical tools  
Instruments

## Static Physico-chemical Properties\*

*Concentration of neutral and ionic species of key nanomaterials*

### Surface attributes of key nanomaterials\*:

- Surface area
- Composition, location, and degree of coverage of surface species
- Morphology from the atomic to cellular scales
- Surface charge

\*Controlled dispersion is critical for all measurements

## Dynamic Physico-chemical Properties\*

*Transformation processes for key nanomaterials\*:*

- Aggregation and agglomeration
- Ionic dissolution
- Adsorption of organic matter and bioconstituents
- Electron transport, e.g., oxidation
- Attachment of nanomaterials to surfaces

### Transport

**Fate:** equilibrium state, concentration, and distribution

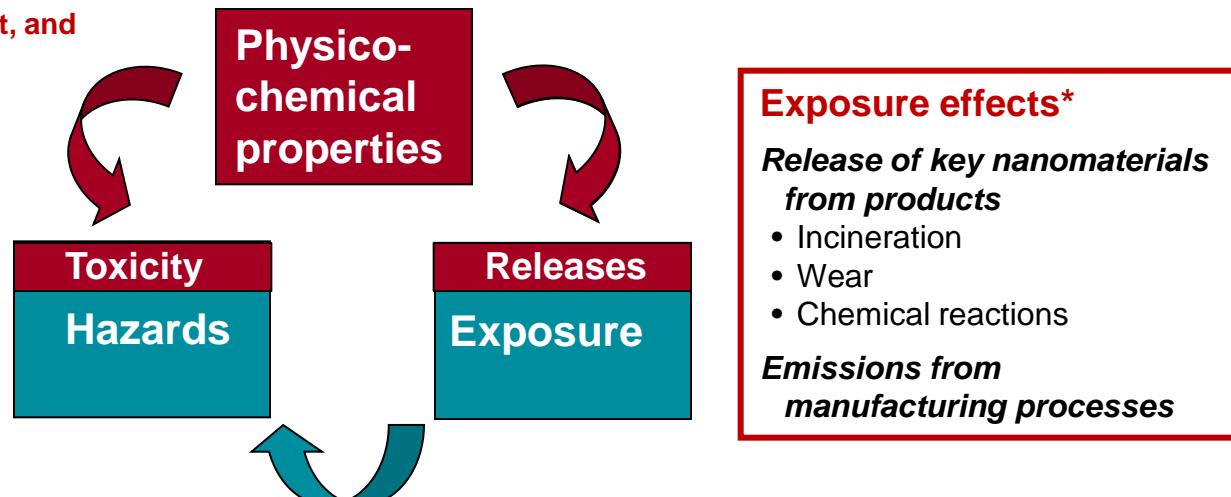
\*In relevant media: air, water, soil, sediment, and biological matrices

## Toxicological Properties\*

*Biomarkers and other indicators of toxicological response*

*Genotoxicity assays*

*Mechanistic cytotoxicity assays*

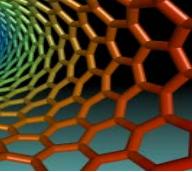


## Exposure effects\*

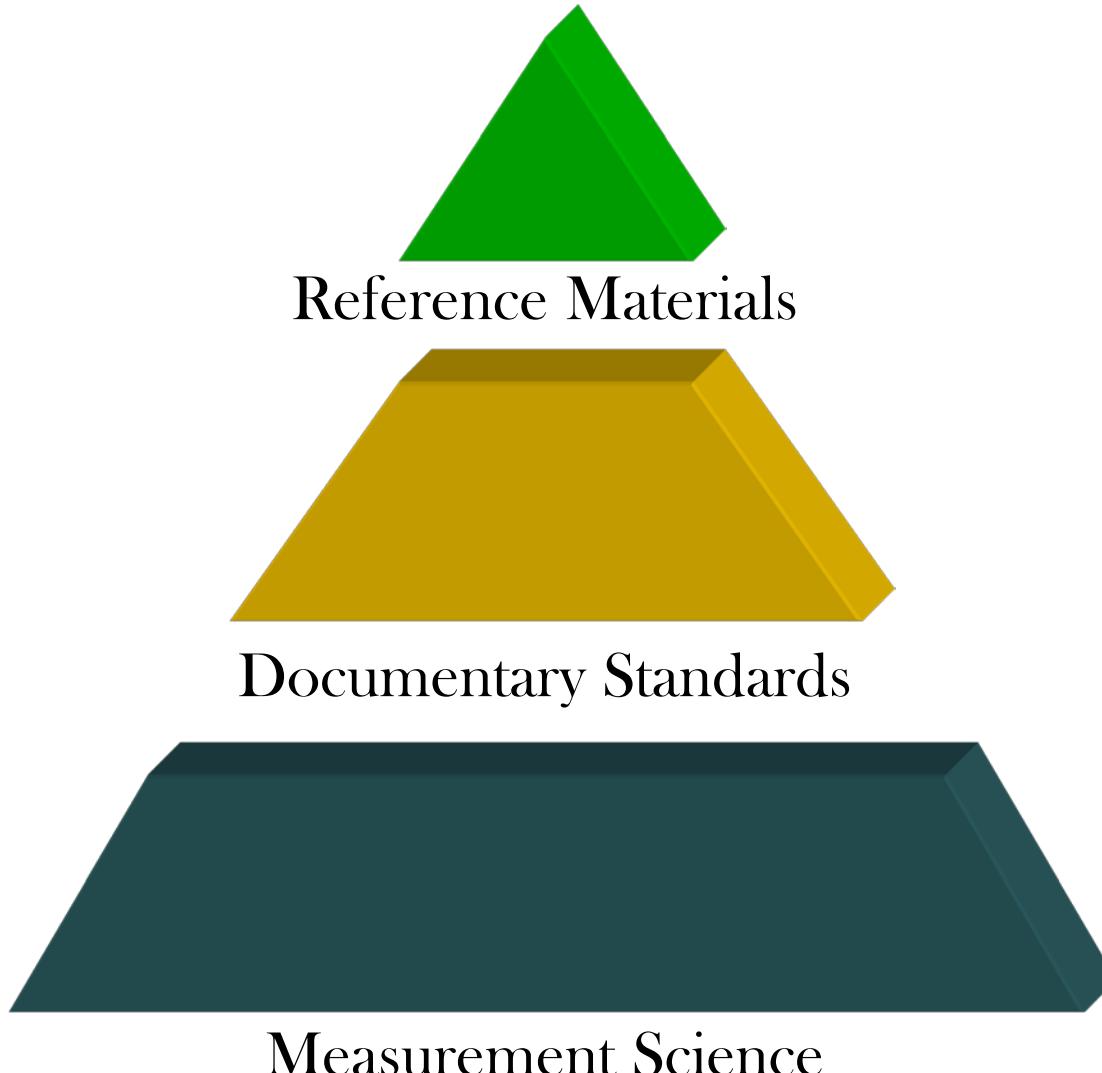
*Release of key nanomaterials from products*

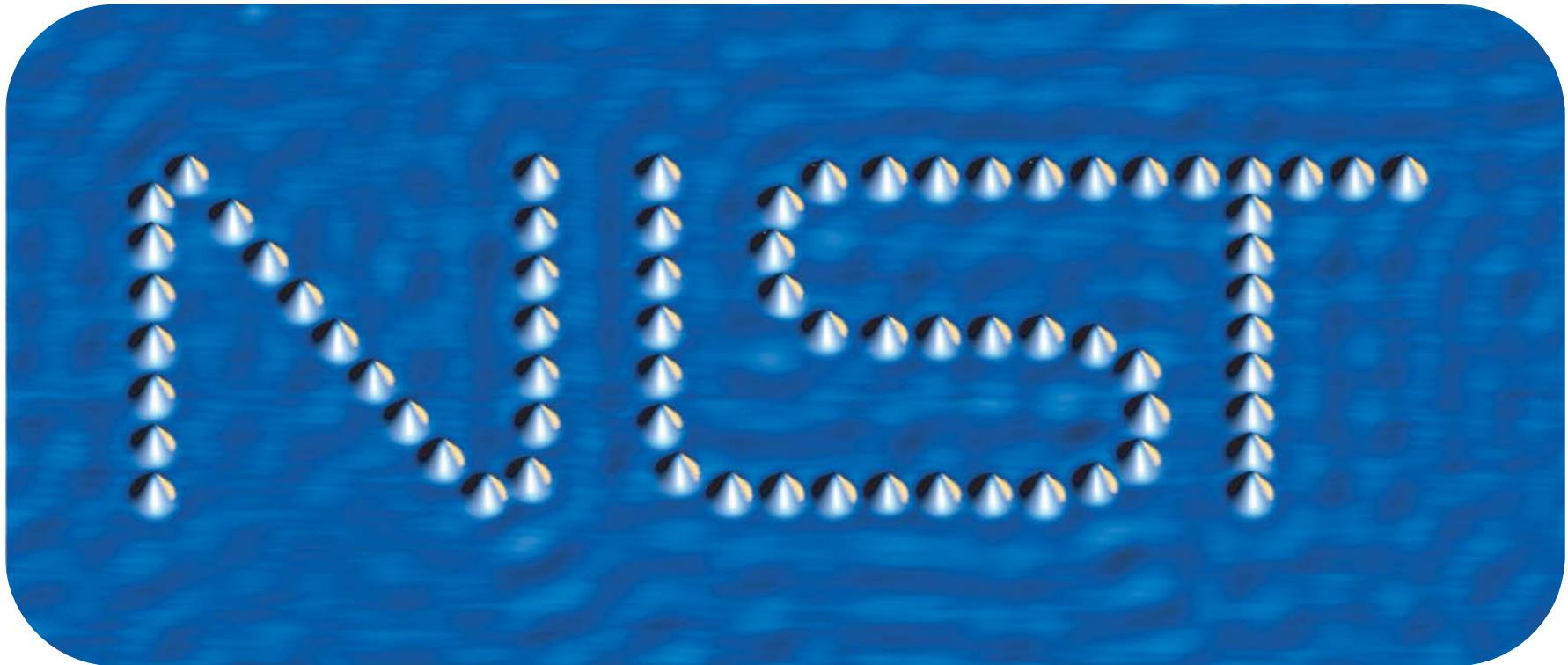
- Incineration
- Wear
- Chemical reactions

*Emissions from manufacturing processes*



# Optimal Approach





Thank you!!