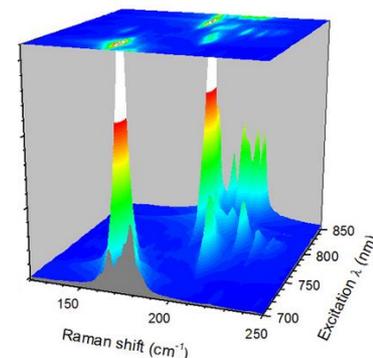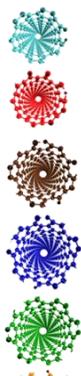# Recent progress in the optical characterization of carbon nanotubes

Yanmei Piao

National Institute of Standards and Technology
Gaithersburg, MD

Council for Optical Radiation Measurements (CORM)
2016 Annual Technical Conference
Special Session: Emerging Professionals
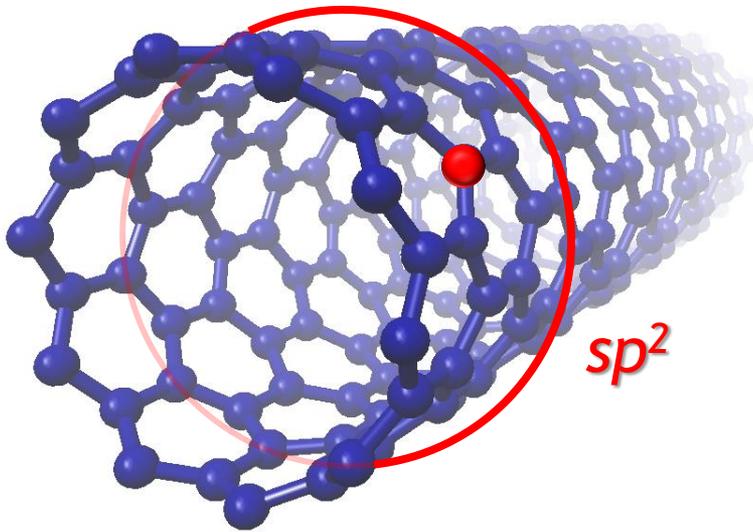May 15, 2016
Gaithersburg, MD

National Institute of Standards and Technology (NIST)
Gaithersburg, MD

Photos taken by Y. Piao

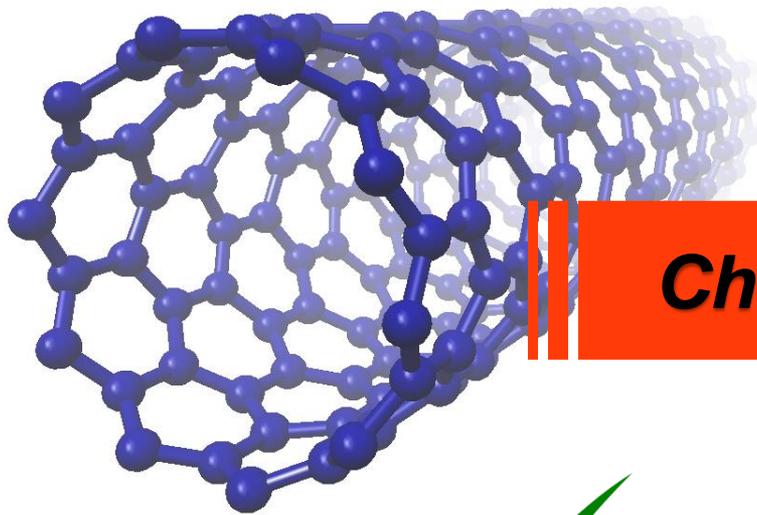# What is a single wall carbon nanotube? (SWCNT)

sp²

- sp^2 carbon lattice
- Seamless hollow cylinder
- Consist only of surface atoms

- Mechanical strength
- Conductivity along the tube axis

- Quantum confinement along the circumference

- Unique optical properties (photoluminescence, Raman, etc.)

What carbon nanotubes can do?

Challenges

Electronics

Shulaker et al. Nature 2013

Medical

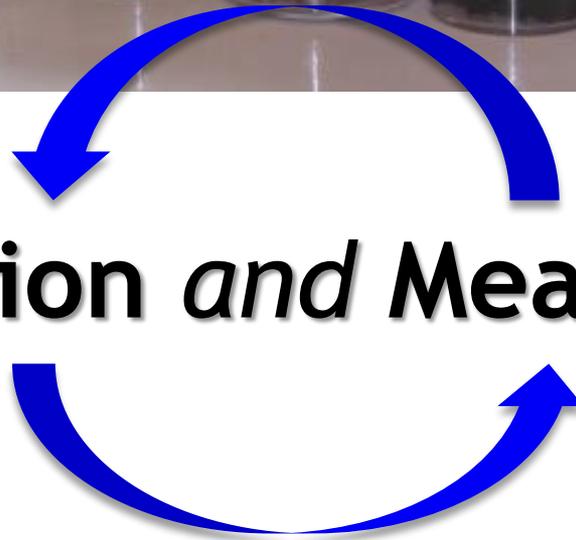Welsher et al. PNAS. 2010
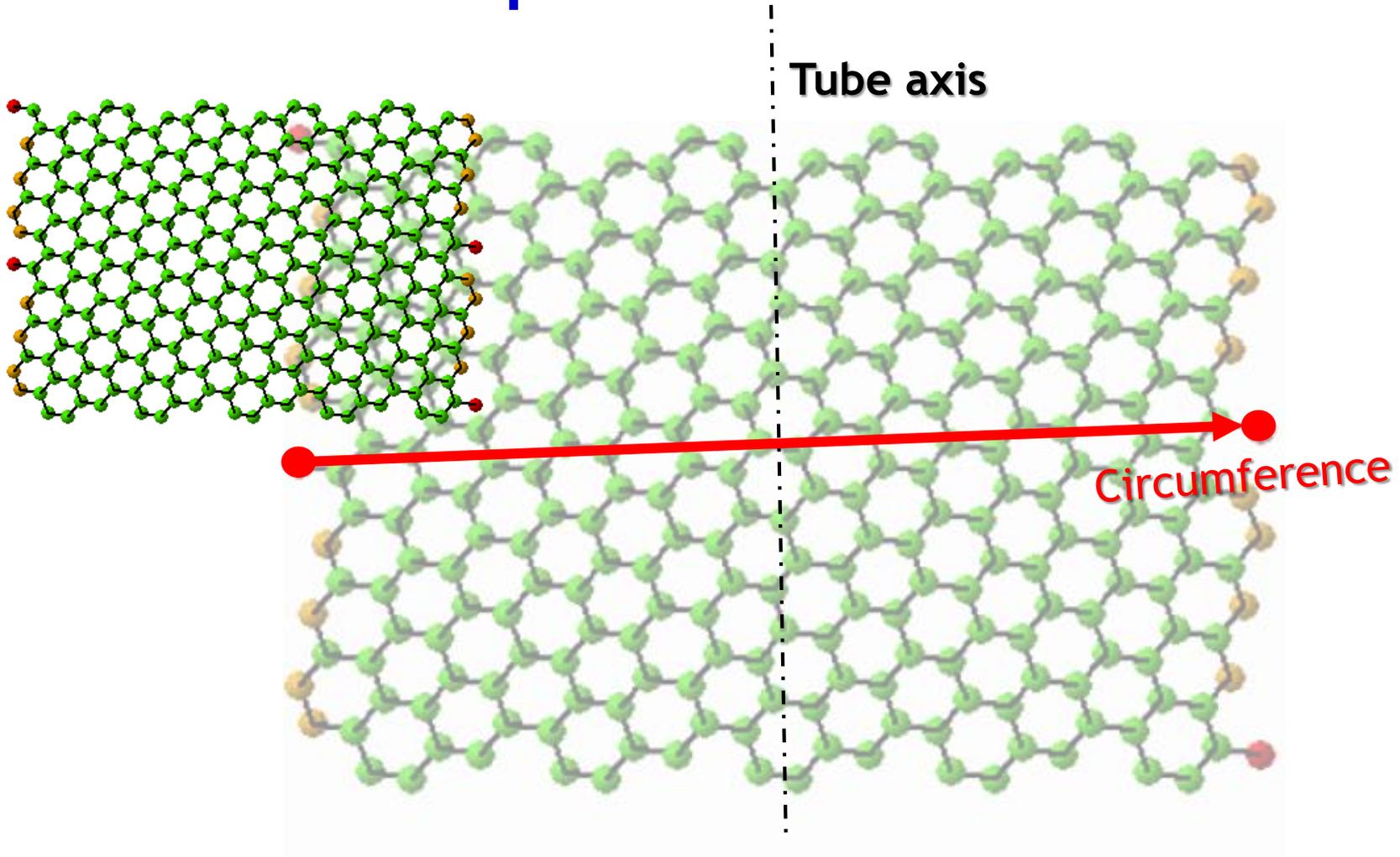
Display

Fraunhofer IPA

Composites

http://www.theguardian.com/nanotechnology-world/carbon-nanotubes-tiny-revolution

From J. Fagan

Hundreds of stable SWCNTs

Separation *and* Measurement

Microscopic Structure of SWCNTs

Tube axis

Circumference

Microscopic structure of SWCNTs

How the graphene sheet rolled up

↓

Structure of SWCNTs:
(d_t, *chiral angle θ*)

Name of a specific SWCNT
Chiral index (n,m)

GIF from http://www.photon.t.u-tokyo.ac.jp/~maruyama/index.html

Electronic properties of SWCNTs

Tube axis
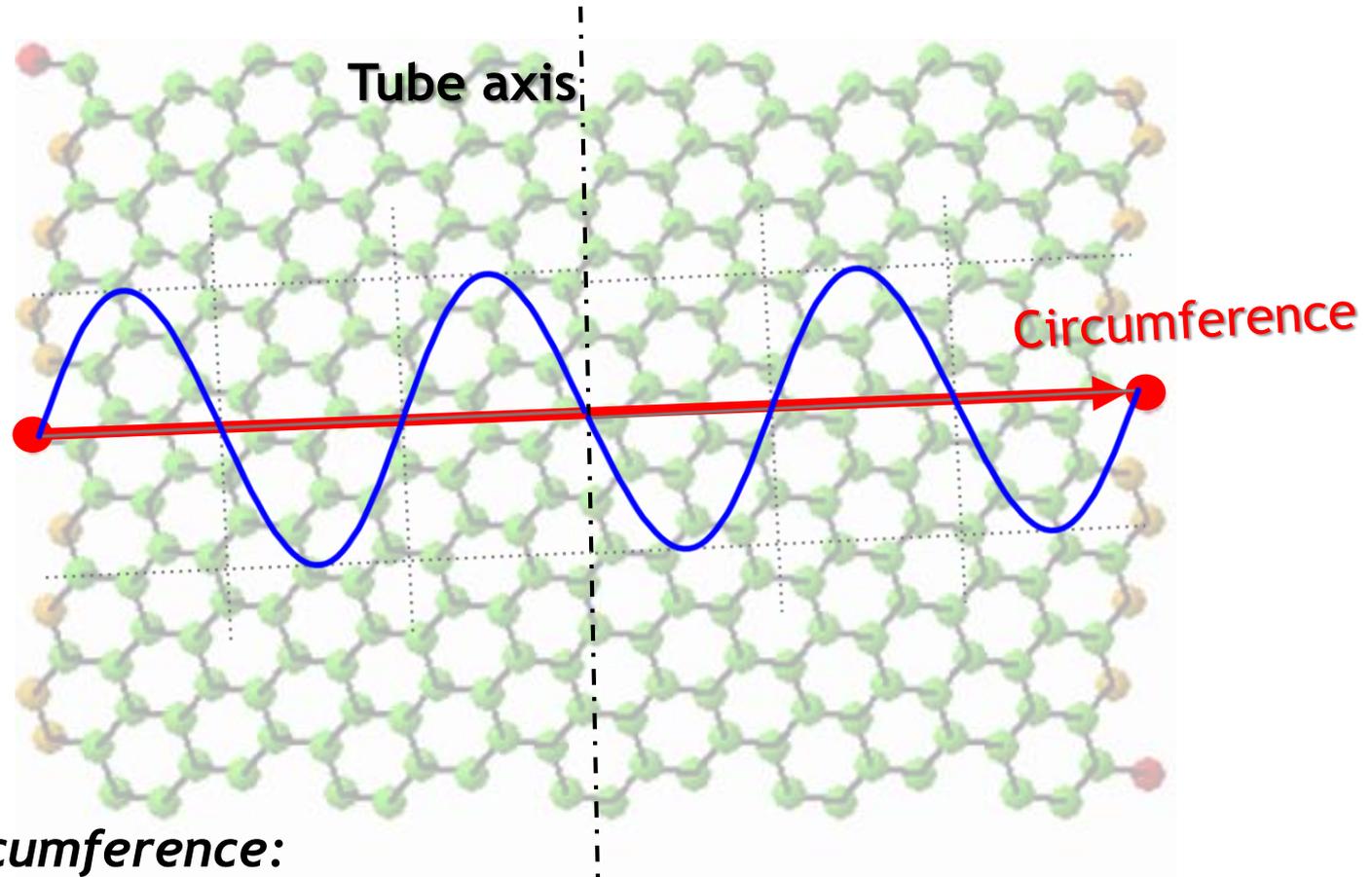
Circumference

Circumference:
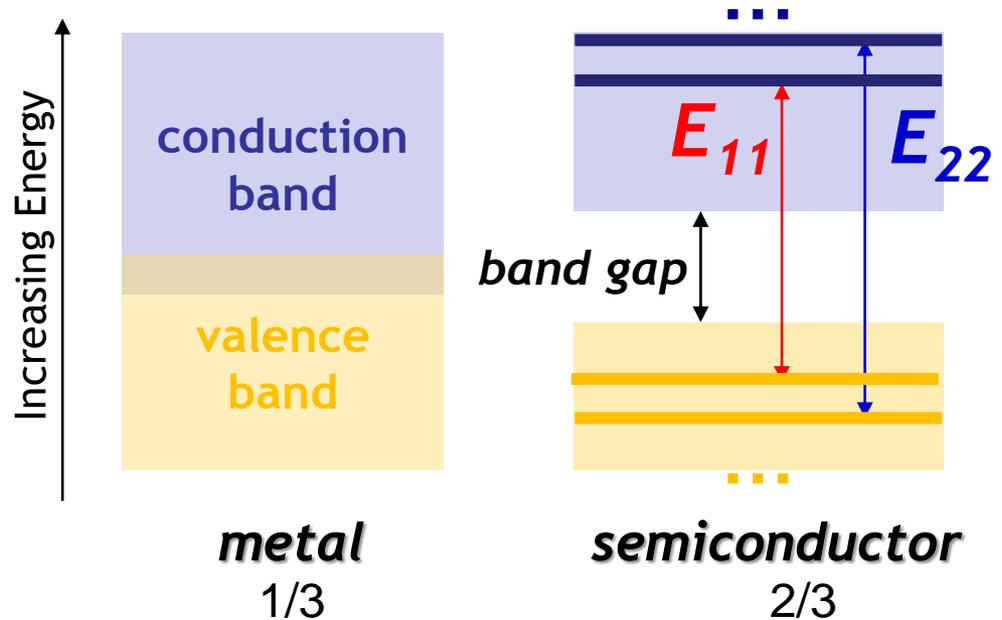
periodic boundary condition $\lambda = \pi$ diameter/a (a integer)

(n,m) determines the physical and electronic structure of SWCNTs
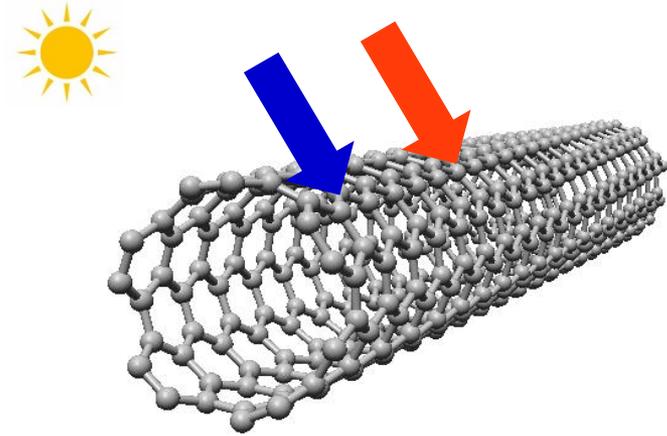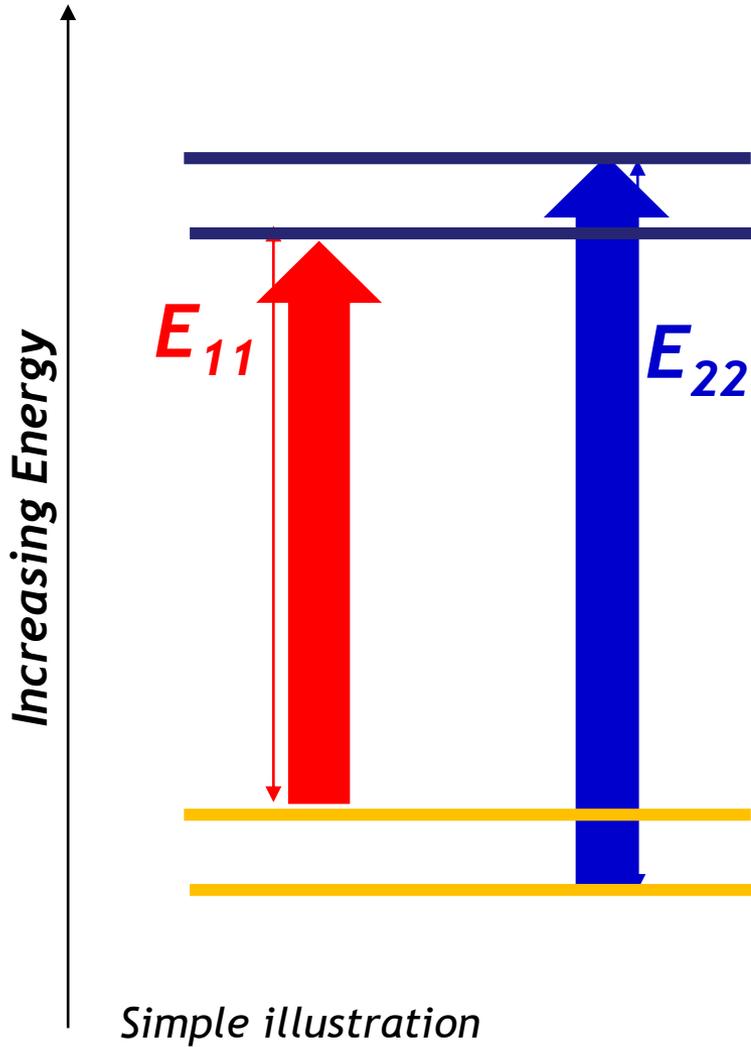
Microscopic structure
(d_t, θ)

Increasing diameter

(n,m)

Electronic types

Increasing Energy

conduction band

valence band

band gap

E_{11} E_{22}

metal
1/3

semiconductor
2/3

Optical properties of SWCNTs
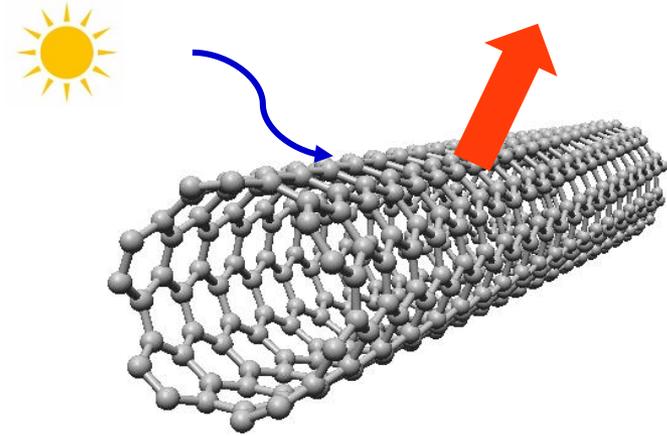

Increasing Energy

E_{11}

E_{22}

Simple illustration
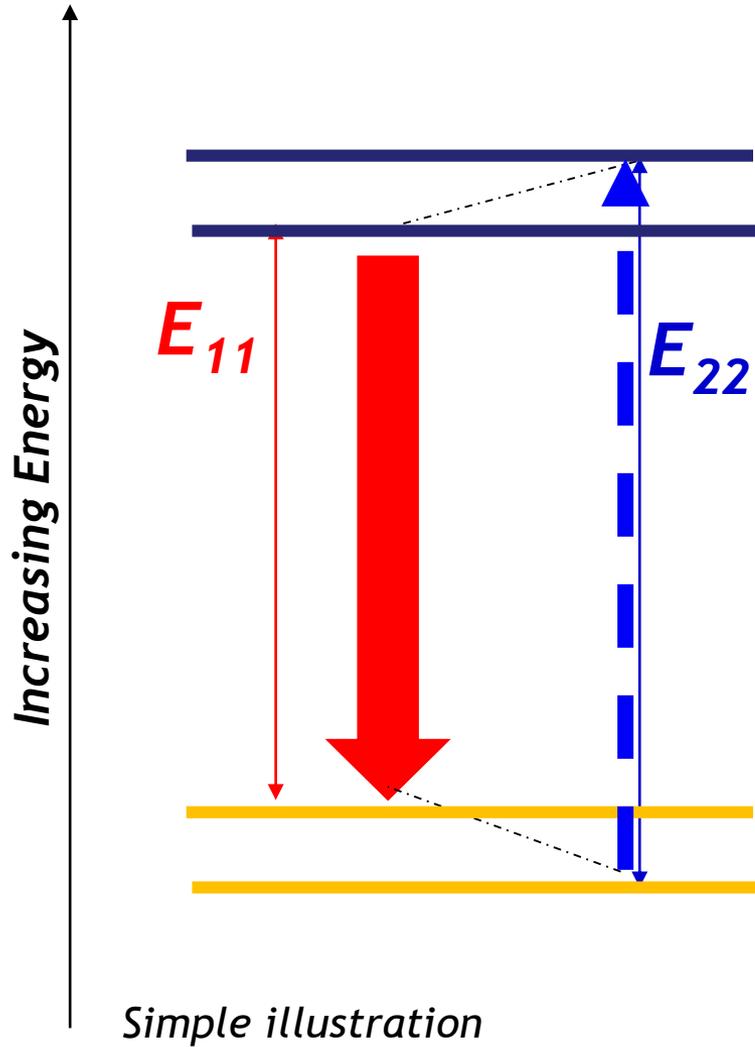
SWCNT absorb light from UV to NIR – (*n,m*) dependent

They can be seen and identified *via*

absorption spectroscopy

Optical properties of SWCNTs

E_{11}

E_{22}
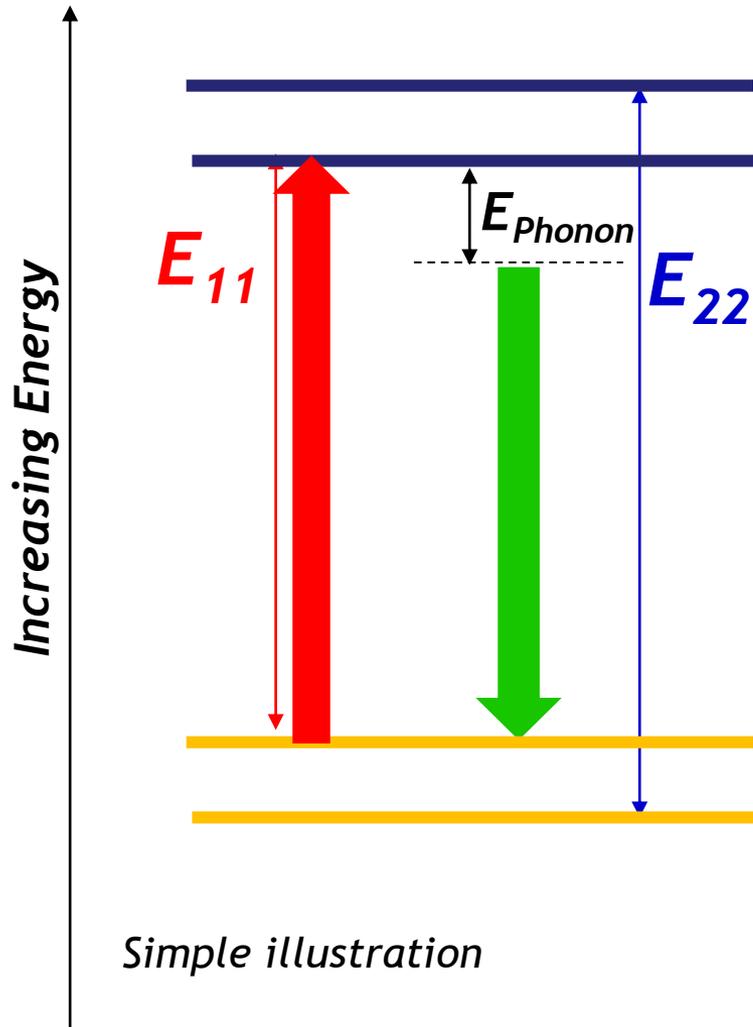
Increasing Energy

Simple illustration

SWCNT emit light from
vis to NIR – (*n,m*) dependent

They can be seen and identified
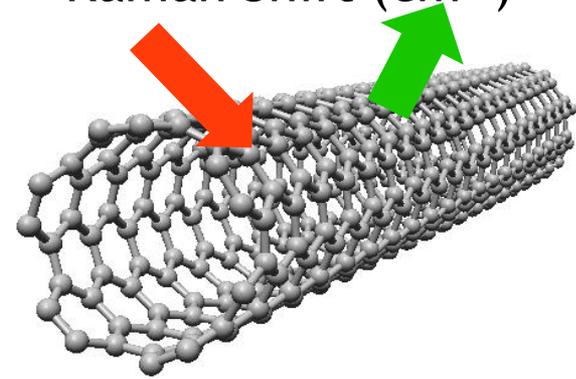*via*
**photoluminescence
spectroscopy**
(not metals)

Optical properties of SWCNTs

Excitation *E* matches E_{11} or E_{22}

Increasing Energy
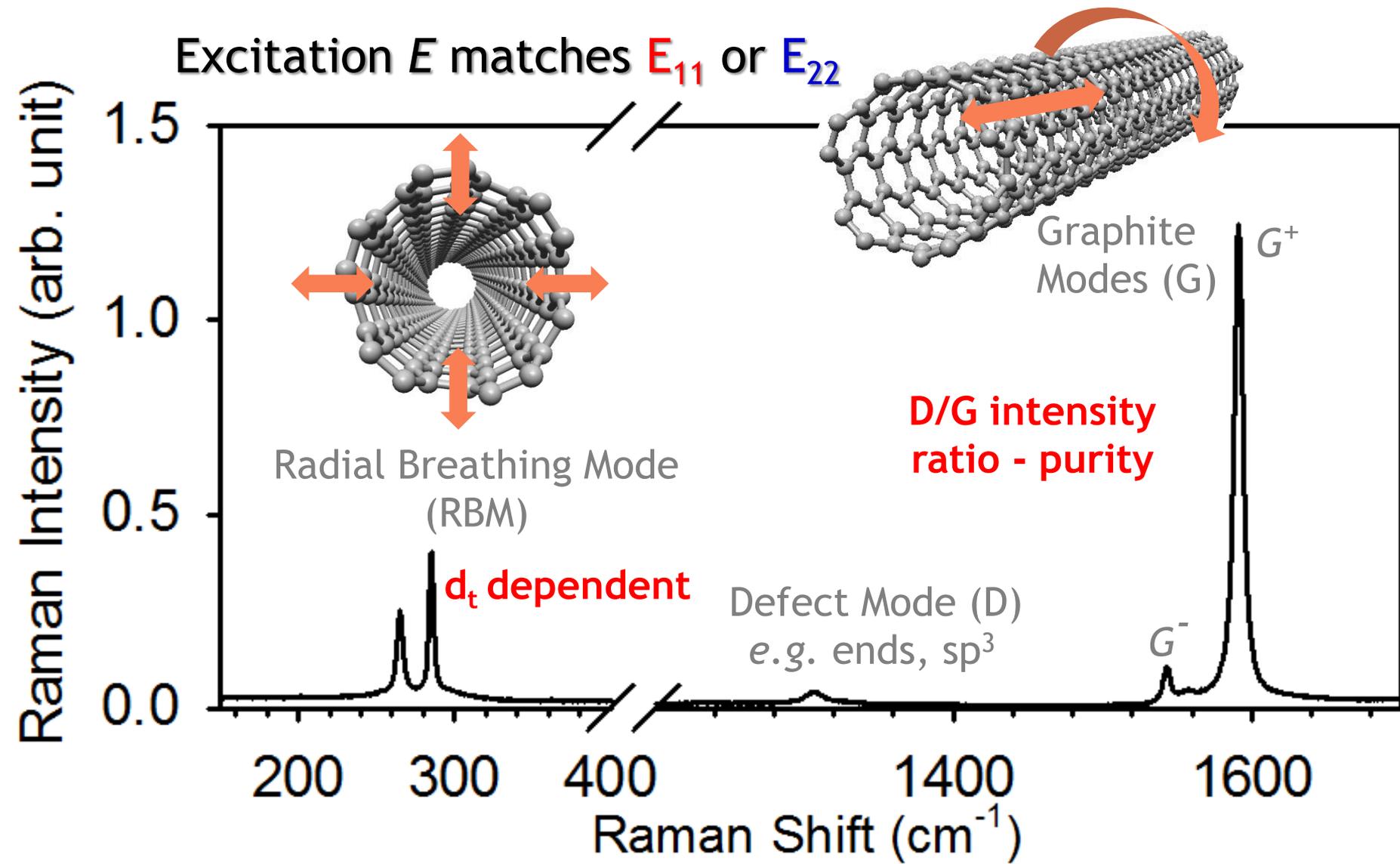
E_{11}

E_{22}

E_{Phonon}

Simple illustration

ΔE ~phonon energy
Raman Shift (cm^{-1})

## Resonant Raman spectroscopy

- Rapid, non-destructive
- Rich
  - Defects/Edges
  - Electron Phonon coupling
  - Temperature
  - Doping
  - Chemical functionalization

Resonant Raman spectroscopy of SWCNTs

Excitation *E* matches E_{11} or E_{22}

Graphite Modes (G)

G^+

G^-

Radial Breathing Mode (RBM)

d_t dependent

D/G intensity ratio - purity

Defect Mode (D) *e.g.* ends, sp³

Raman Intensity (arb. unit)

Raman Shift (cm⁻¹)

Separation of SWCNTs:
Aqueous-two-phase extraction technique
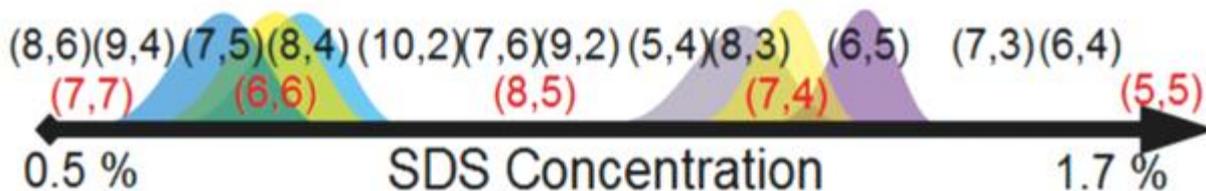
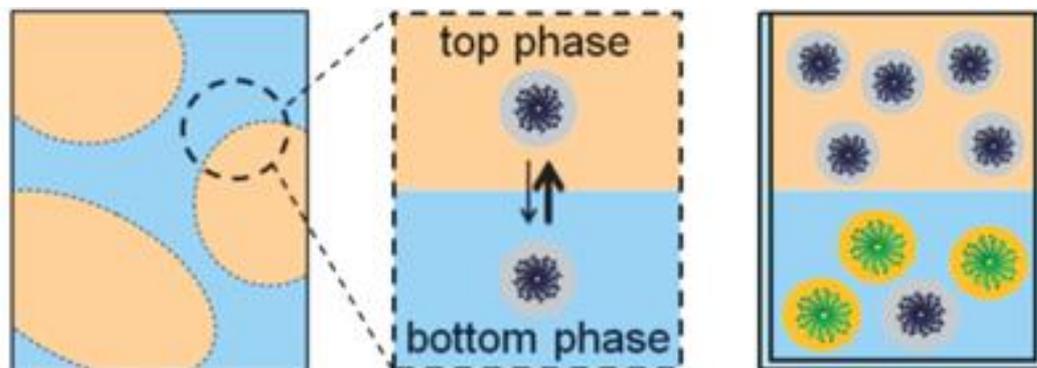**ATPE technique was pioneered at NIST**
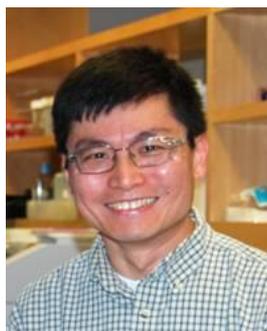
Dr. Jeff Fagan   Dr. Ming Zheng

JACS **2013**, *135*, 6822
JACS **2014**, *136*, 10383
Adv Mater **2014**, *18*, 2800
ACS Nano, **2015**, 9, 5377

PEG

Dextran + Dispersant Layer

top phase

bottom phase

(8,6)(9,4)(7,5)(8,4) (10,2)(7,6)(9,2) (5,4)(8,3) (6,5) (7,3)(6,4)
(7,7)   (6,6)   (8,5)   (7,4)   (5,5)

0.5 %   SDS Concentration   1.7 %

DOC Concentration fixed: 0.04%
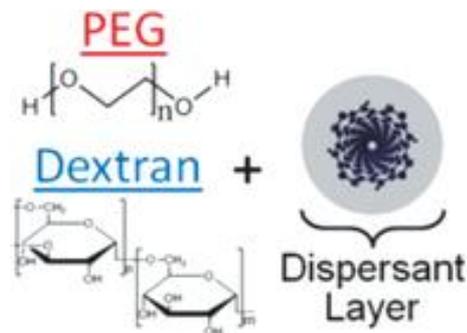
(n,m) separated SWCNTs

8 single chirality enriched, 3 few chirality enriched SWCNTs

(5,4) (6,4) (7,3) (6,5) (8,3) (10,0)* (9,2)* (7,5) (8,4) (7,6)* (11,1)

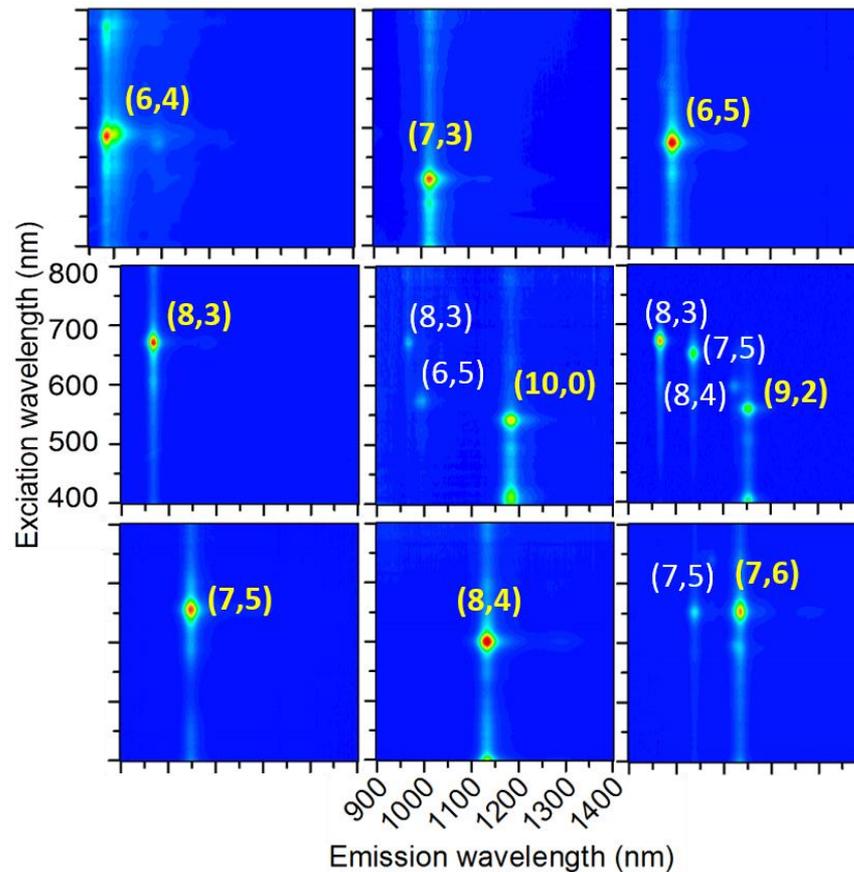*Increasing diameter*

0.6 nm — 0.9 nm
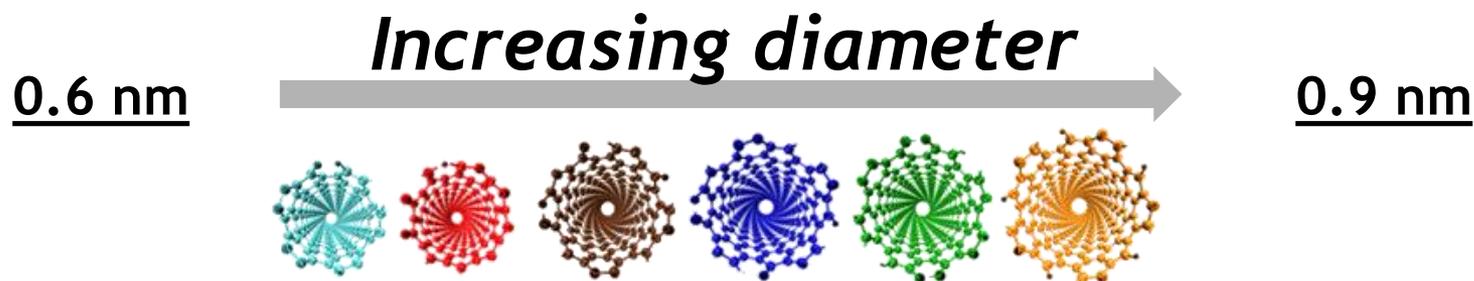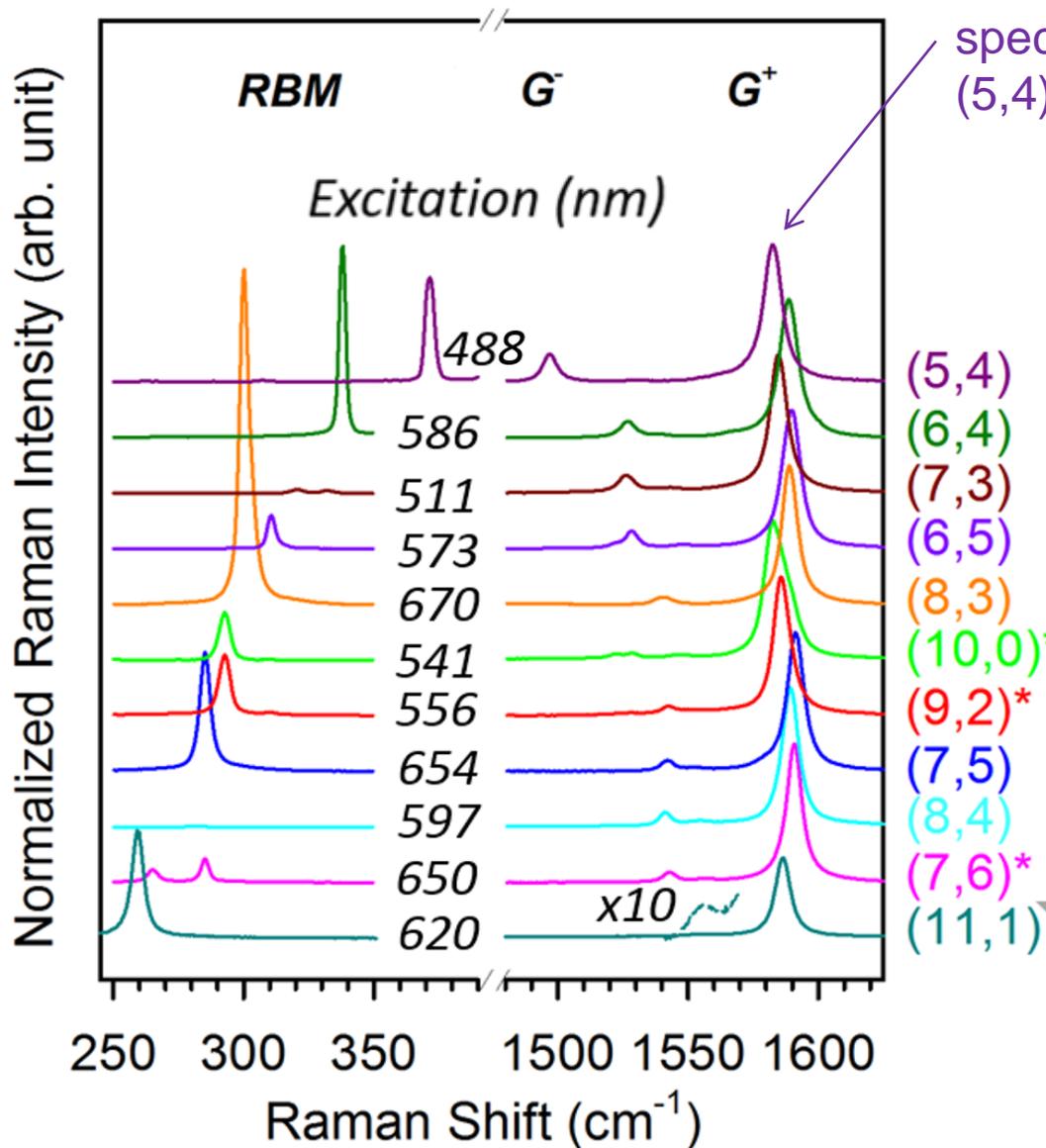
(n,m) separated SWCNT characterization

UV-vis-NIR
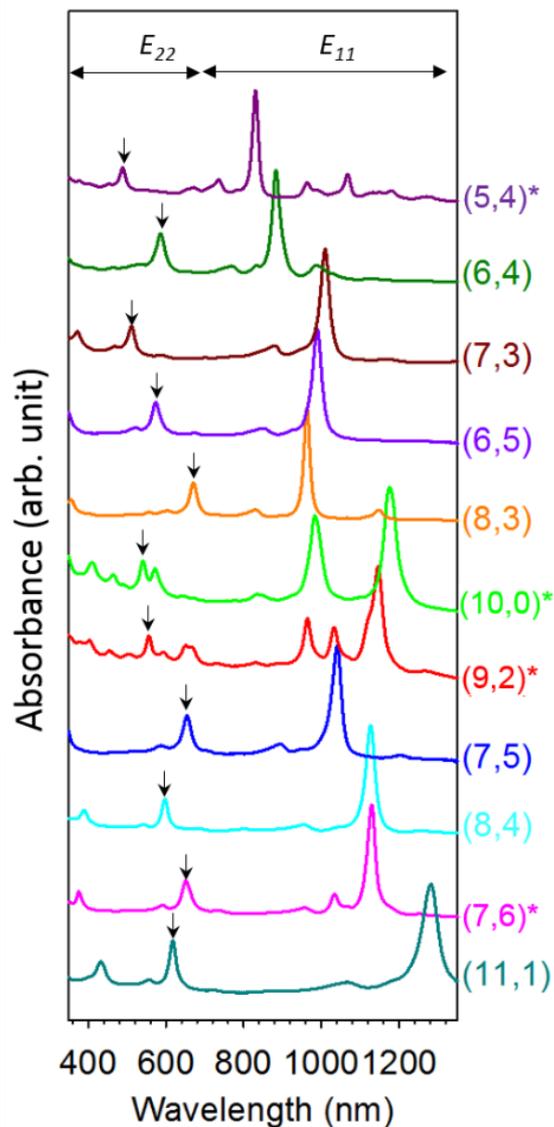
Photoluminescence Excitation

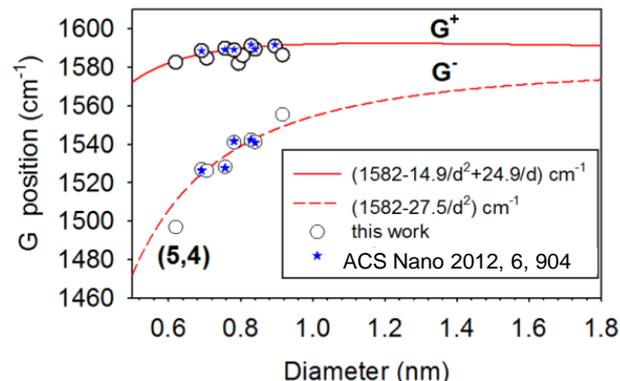# Dramatic variance in Raman intensity of SWCNTs

First resonance Raman spectrum of enriched (5,4)solution (_0.62 nm_)

- RBM is (n,m) dependent
- G is independent of (n,m)
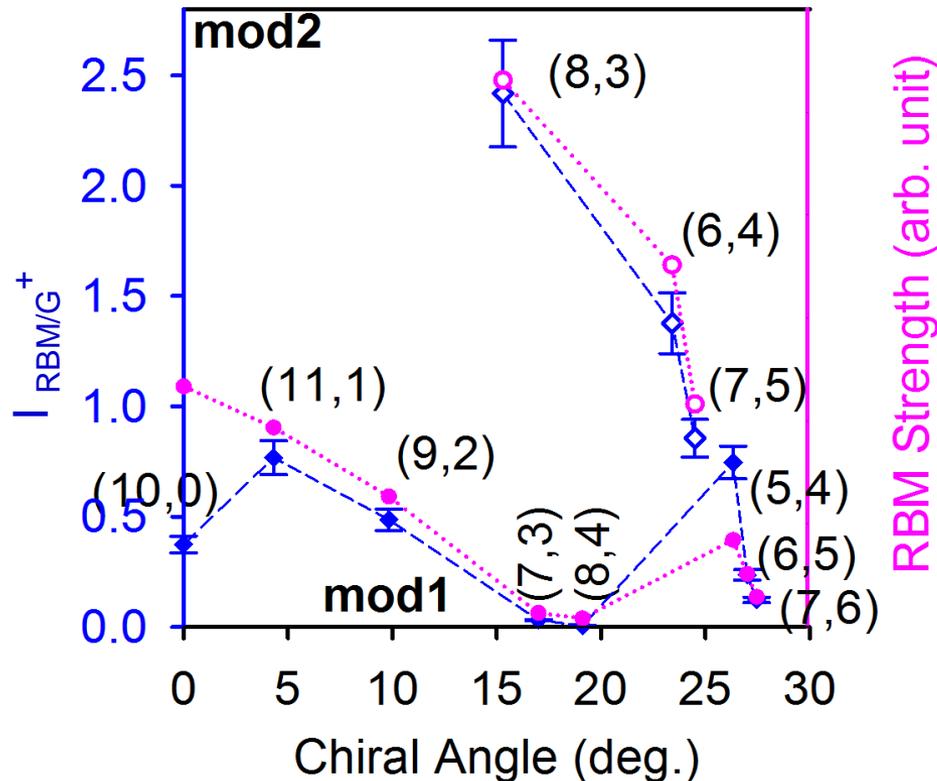- E_{22} Resonant Raman spectra with tunable dye laser

Extended the available G⁻ and G⁺ vs diameter data to cover more of the smaller diameter regime

(n,m) dependent Raman intensity

RBM intensity *vs.* chiral angle

Prediction in 2004
*Popov. et al. Nano Lett.*

General trends:

- $I_{RBM/G}$: mod2 > mod1
  $(n-m) \div 3$ remainder 1 or 2

- mod1 has a valley at ~20°

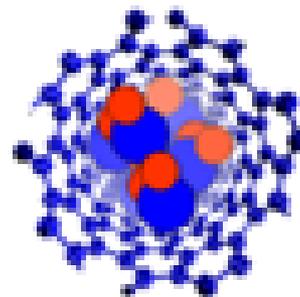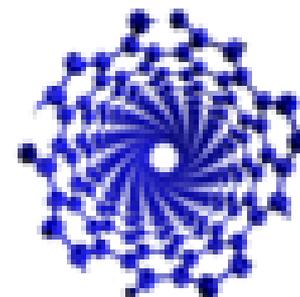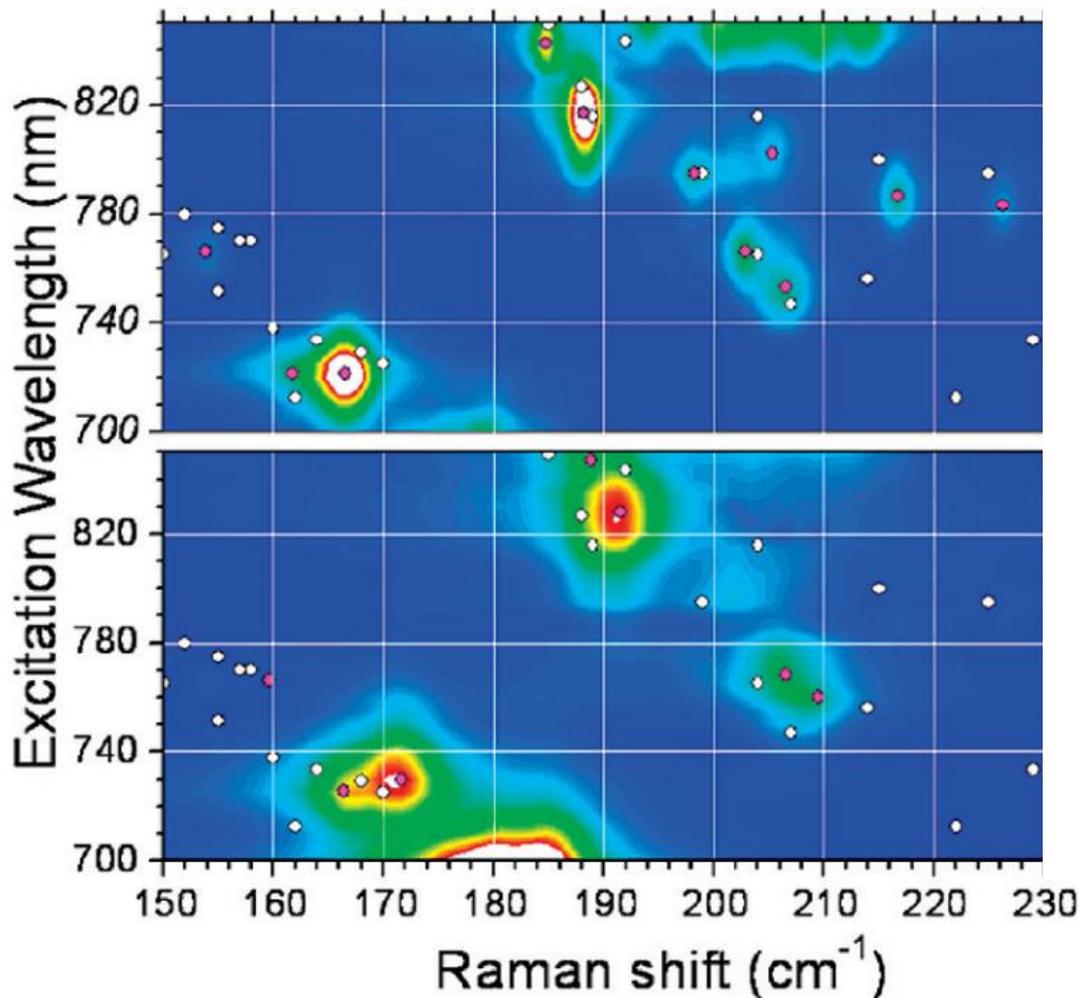**Experiment results match with prediction!**

Tabulated data

Dominant (n,m)	mod	Surfactant	d_t^Δ (nm)	θ (deg.)	Observed					
					$E_{22}^\S$ (nm)	RBM (cm^{-1})	G$^-$ (cm^{-1})	G$^+$ (cm^{-1})	I_{G^-}/I_{G^+}	I_{RBM}/I_{G^+} $
(5,4)*	1	DOC	0.620	26.33	488	372	1497	1583	0.20	0.75
(6,4)	2	DOC	0.692	23.41	586	338	1527	1589	0.12	1.4
(7,3)	1	DNA	0.706	17.00	511	332	1526	1585	0.13	0.021
(6,5)	1	DNA	0.757	27.00	573	311	1528	1590	0.13	0.24
(8,3)	2	DNA	0.782	15.30	670	300	1541	1589	0.048	2.4
(10,0)*	1	DOC	0.794	0.00	541	295	-	1583#	-	0.37
(9,2)*	1	DOC	0.806	9.83	556	293	-	1586#	-	0.49
(7,5)	2	DNA	0.829	24.50	654	285	1542	1591	0.076	0.88
(8,4)	1	DNA	0.840	19.11	597	281	1541	1589	0.094	0.0049
(7,6)*	1	DOC	0.895	27.46	650	265	1543#	1591#	0.068	0.12
(11,1)	1	DNA	0.916	4.31	620	259	1555	1586	0.026	0.75

(8,4) *vs.* (8,3) Raman intensity
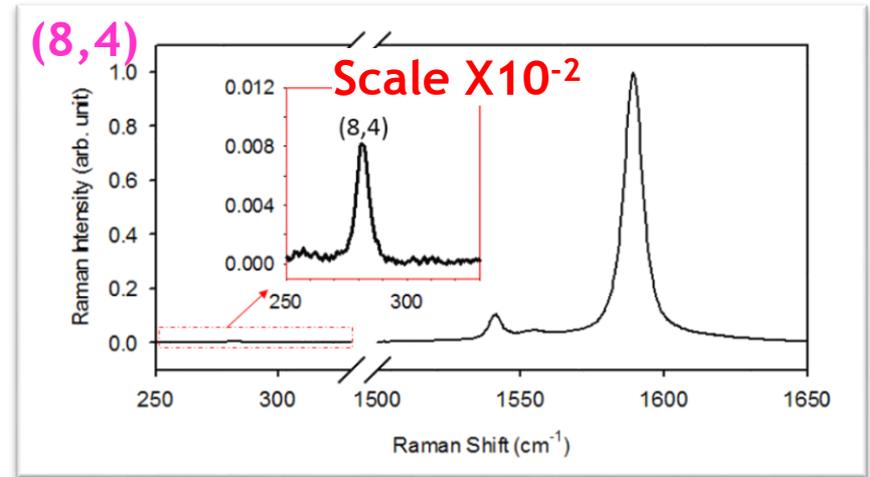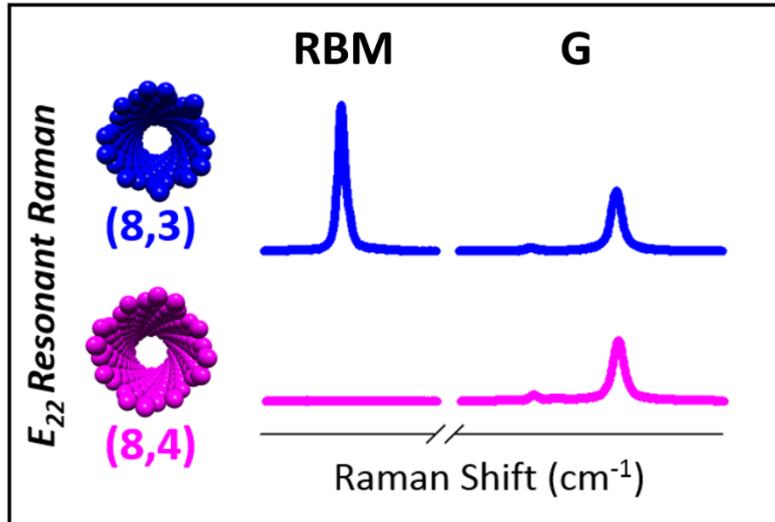
Using Raman as a SWCNT characterization method requires comprehensive understanding of the (n,m) dependency of RBM/G intensity ratio

Water-filled and empty SWCNTs

Raman instrument and laser

Triple Grating Raman Instrument

Ar+ laser

tunable dye lasers

Hight Walker Lab @ NIST

Conclusions

- Demonstrated with chirality enriched samples that E_{22} resonant Raman RBM to G mode intensity ratio is highly chiral angle and mod dependent, in good agreement with theory.

- Established a Raman spectral library is demonstrated to be useful in decoupling multiple species

Optical metrology of SWCNT is important in not only quantitative analysis but also qualitative assessment.
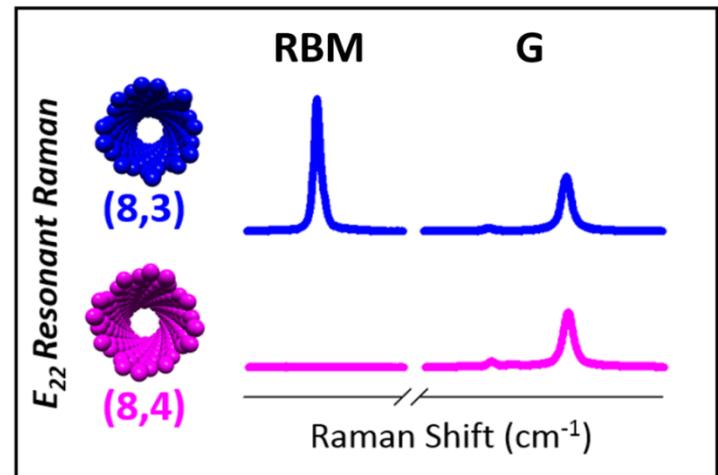
Acknowledgements
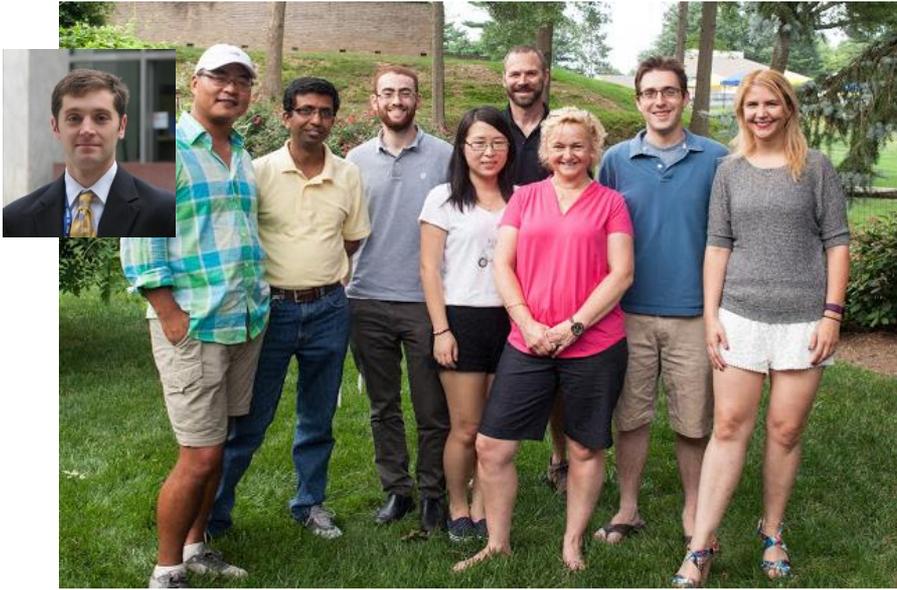
Dr. Angie Hight Walker
&
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Dr. Jeff Simpson
Dr. Jason Streit
Dr. Geyou Ao
Dr. Ming Zheng