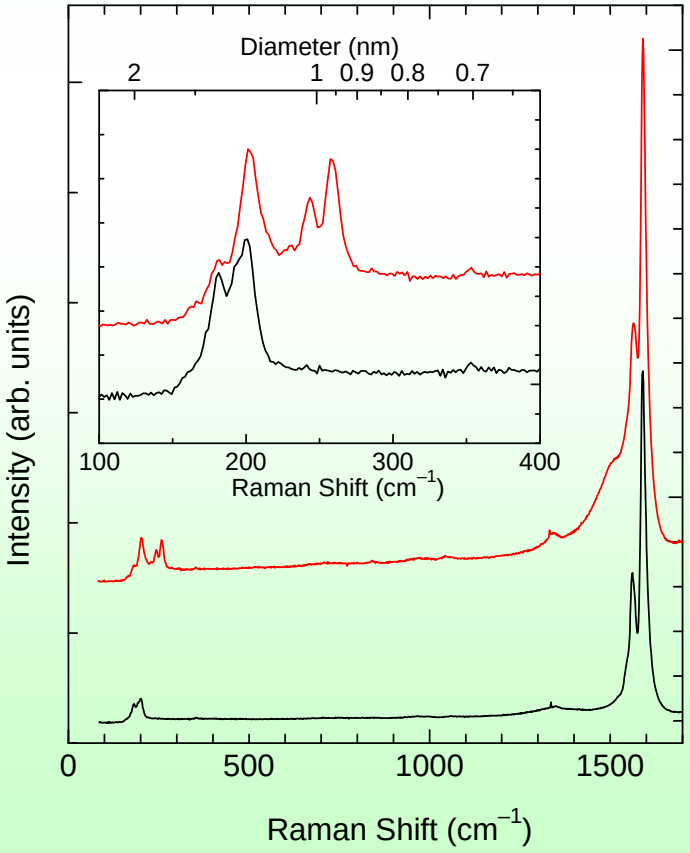
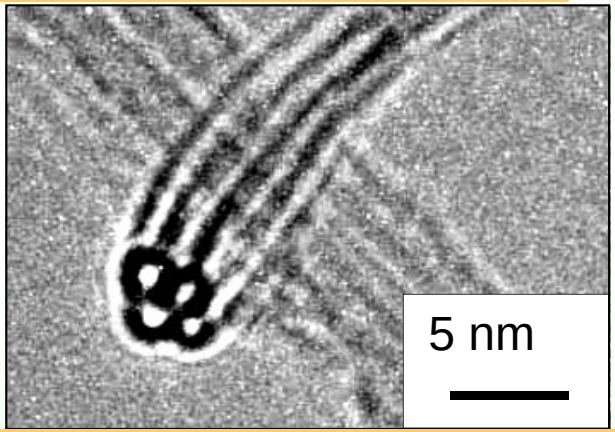
Molecular Thermo-Fluid Engineering 2013

単層カーボンナノチューブとグラフェンの電子顕微鏡観察と分光
Electron Microscopy and Spectroscopy of Carbon Nanotube and Graphene

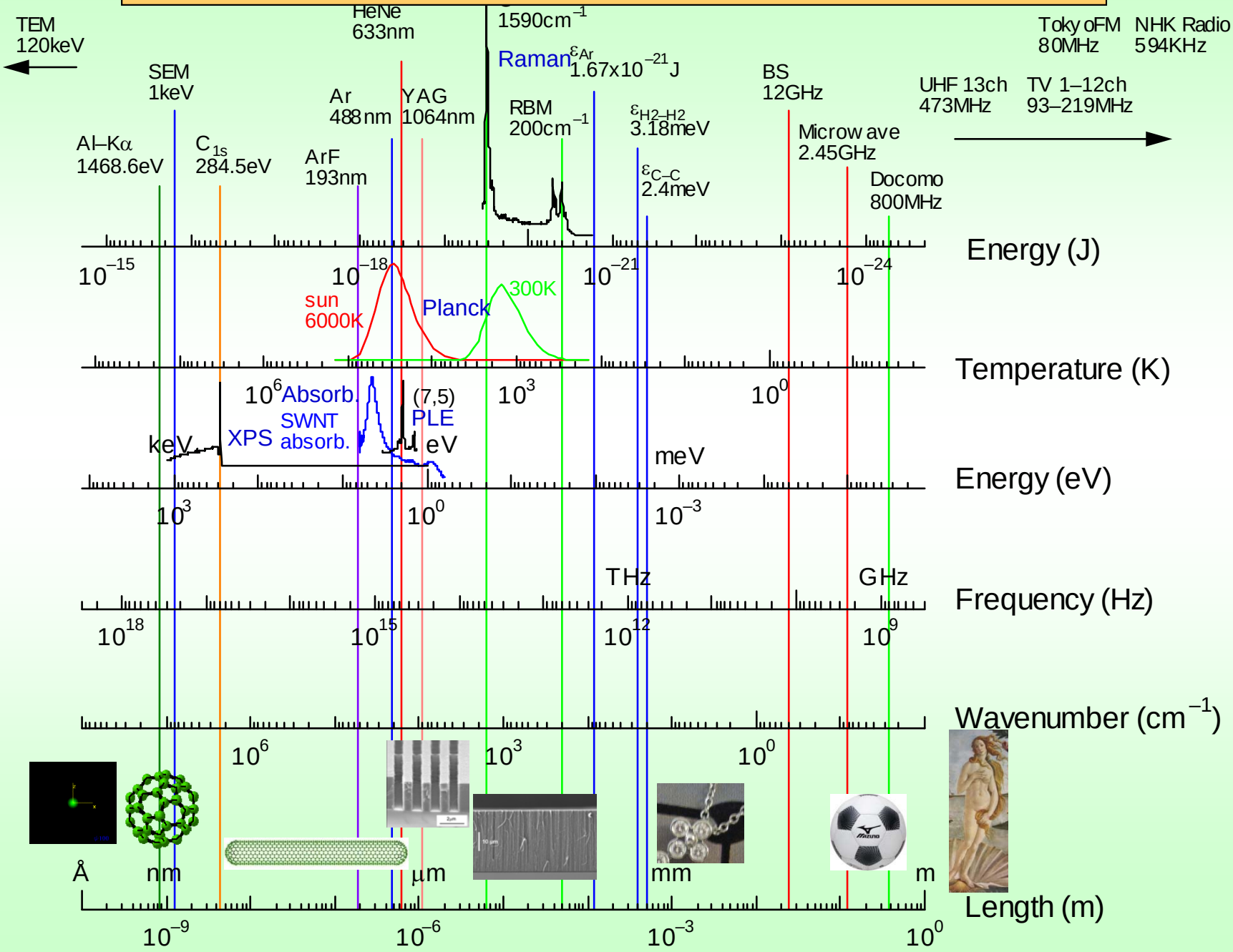




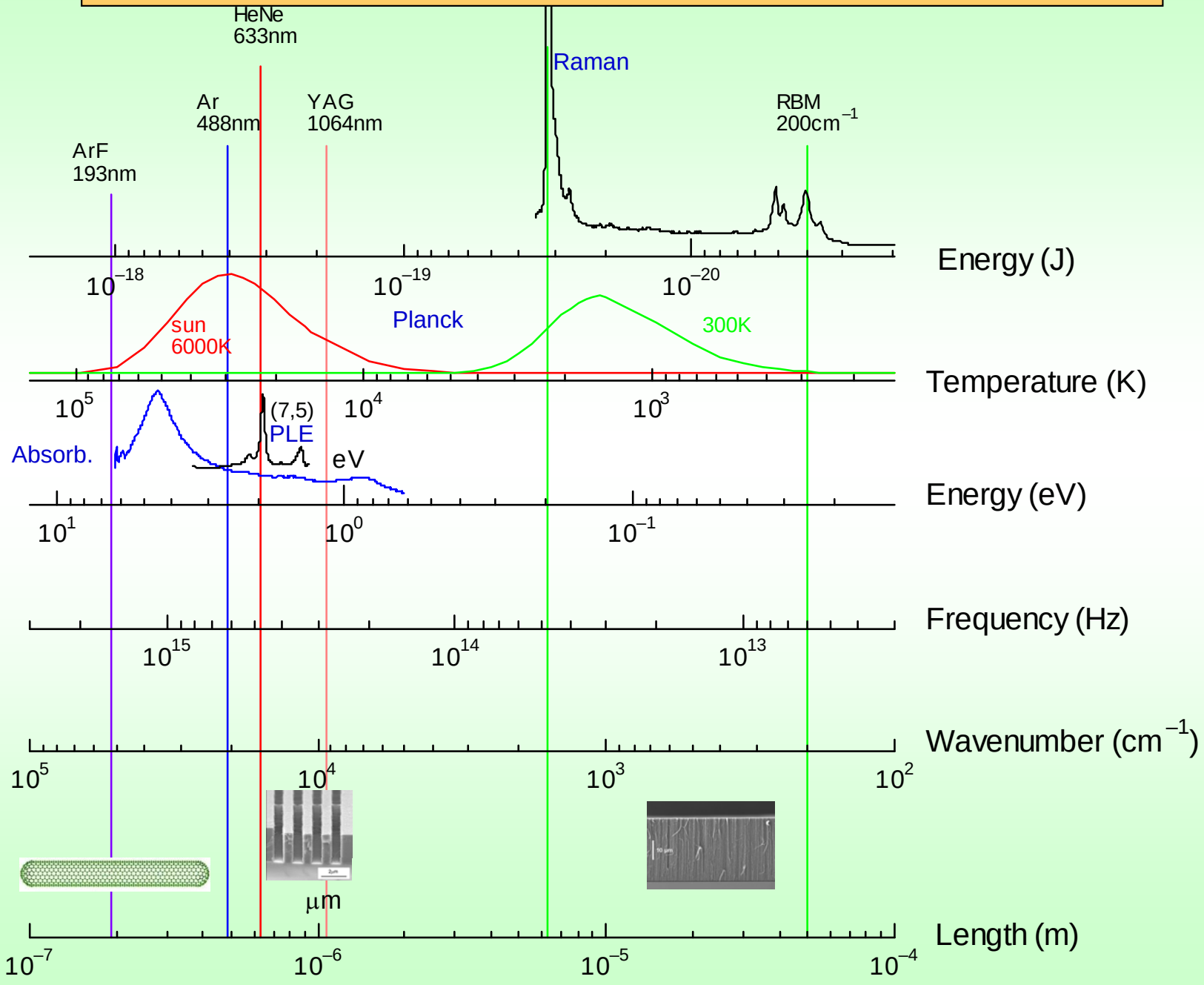
丸山 茂夫
Shigeo Maruyama
東京大学大学院工学系研究科
機械工学専攻

http://www.photon.t.u-tokyo.ac.jp

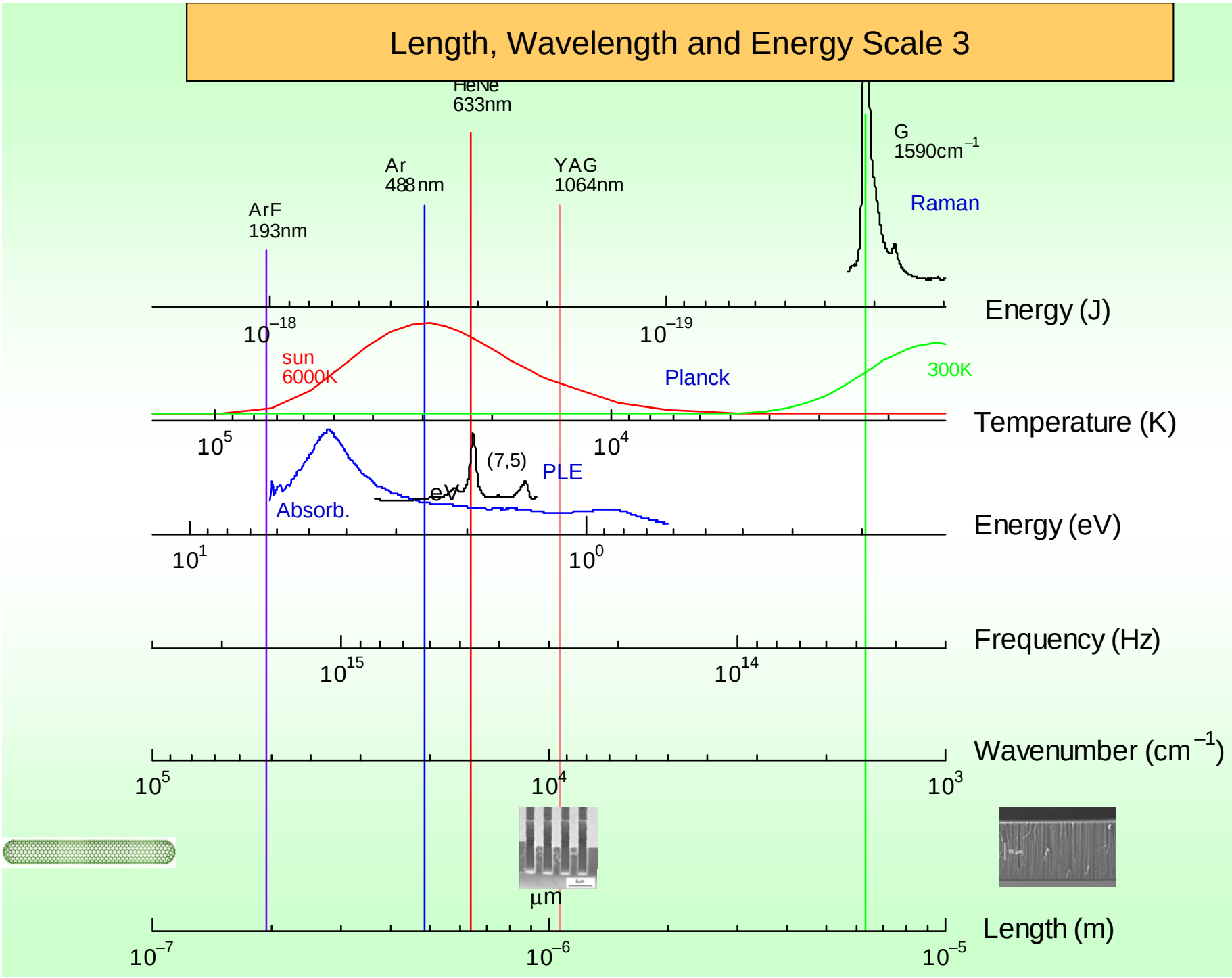
Length, Wavelength and Energy Scale



Length, Wavelength and Energy Scale 2



Length, Wavelength and Energy Scale 3



Characterization of Carbon Nanotubes

Electron Microscopy
- Transmission Electron Microscopy (TEM)
- Scanning Electron Microscopy (SEM)
- Scanning Transmission Electron Microscopy (STEM)

Scanning Probe Microscopy
- Atomic Force Microscopy (AFM)
- Scanning Tunneling Microscopy (STM)

Optical Spectroscopy
- Resonant Raman Scattering
- Absorption Spectroscopy (UV-Vis-NIR)
- Fluorescence Spectroscopy

X-ray
- X-ray diffraction
- X-ray photoelectron spectroscopy (XPS, ESCA)

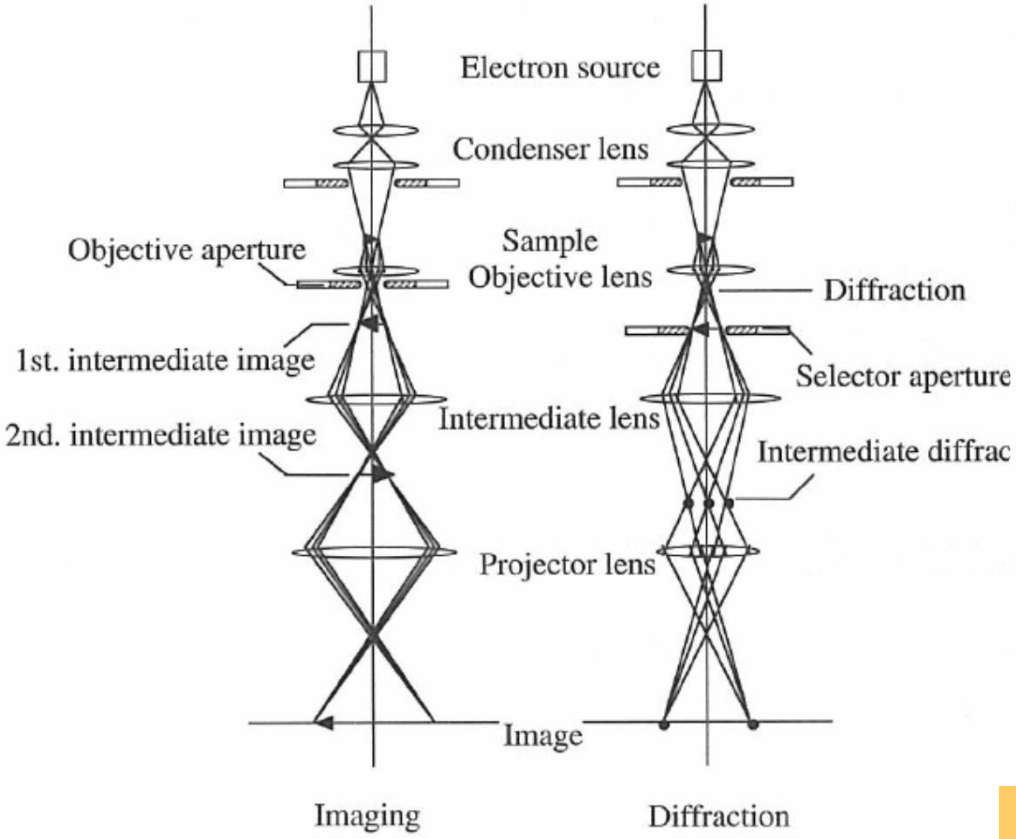
Transmission Electron Spectroscopy

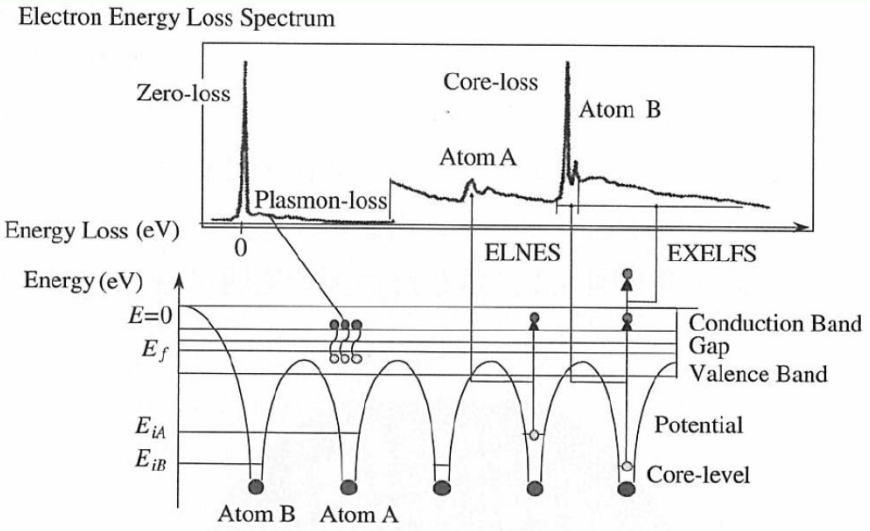
透過型電子顕微鏡(TEM)

高分解能像(Phase contrast)

電子線回折(Electron diffraction)

電子線分光(EELS, Electron energy loss spectroscopy)

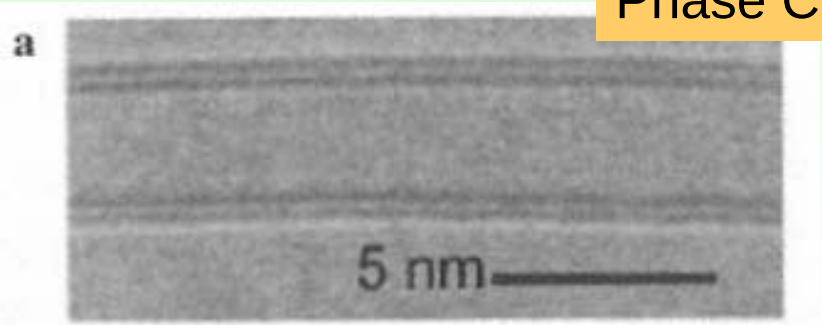


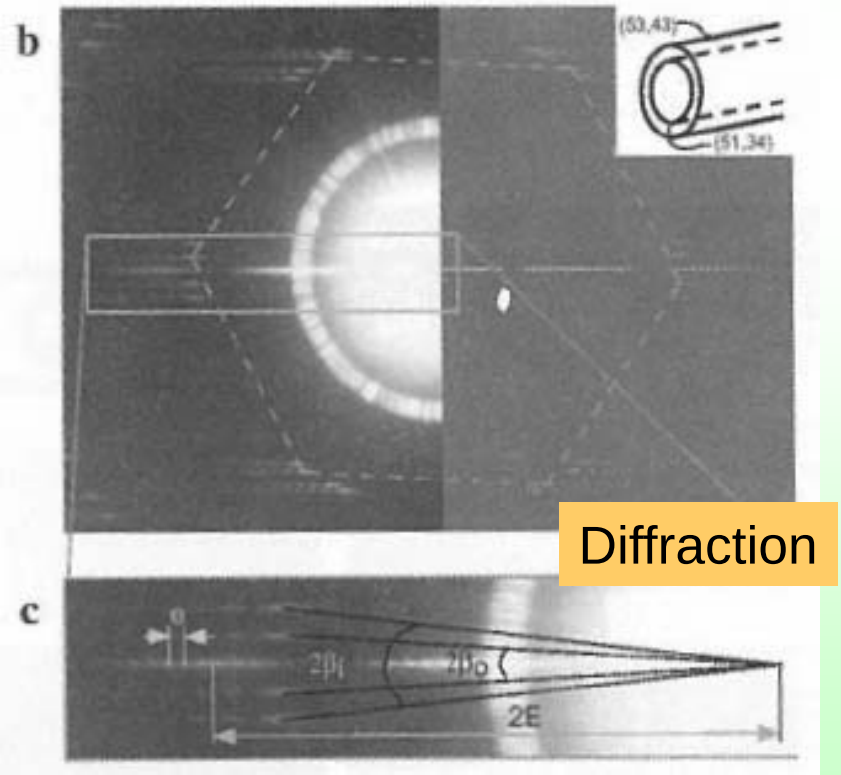


末永和知，カーボンナノチューブの基礎と応用，培風館

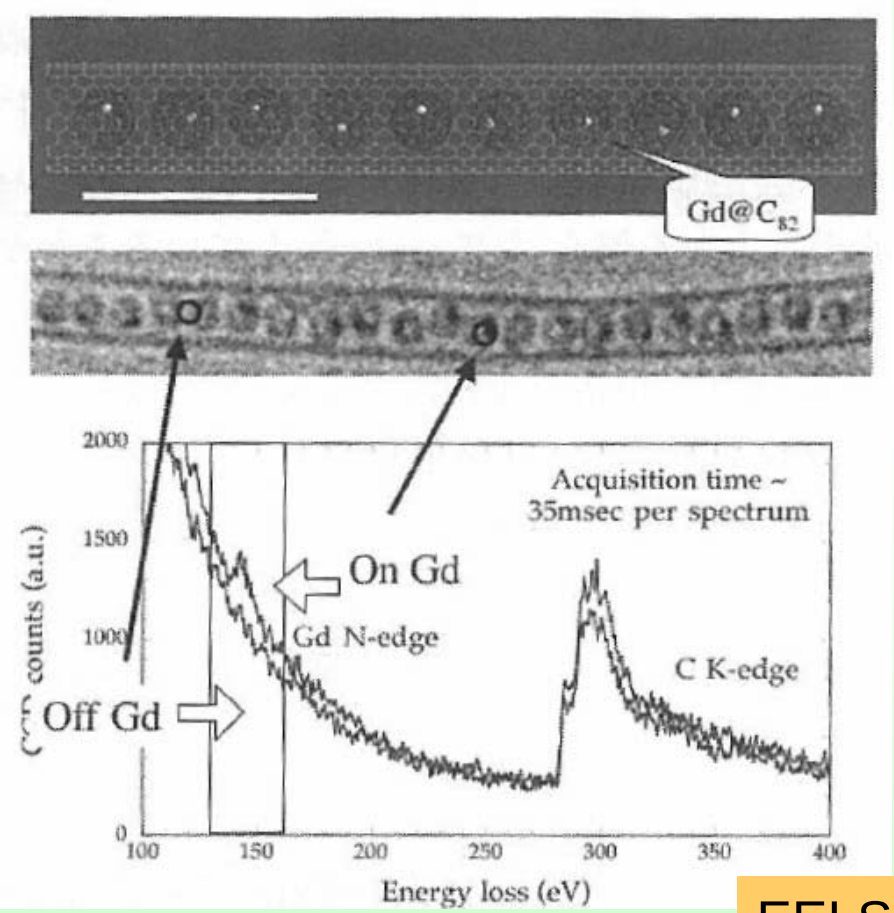
Transmission Electron Spectroscopy

Phase Contrast





Diffraction



EELS

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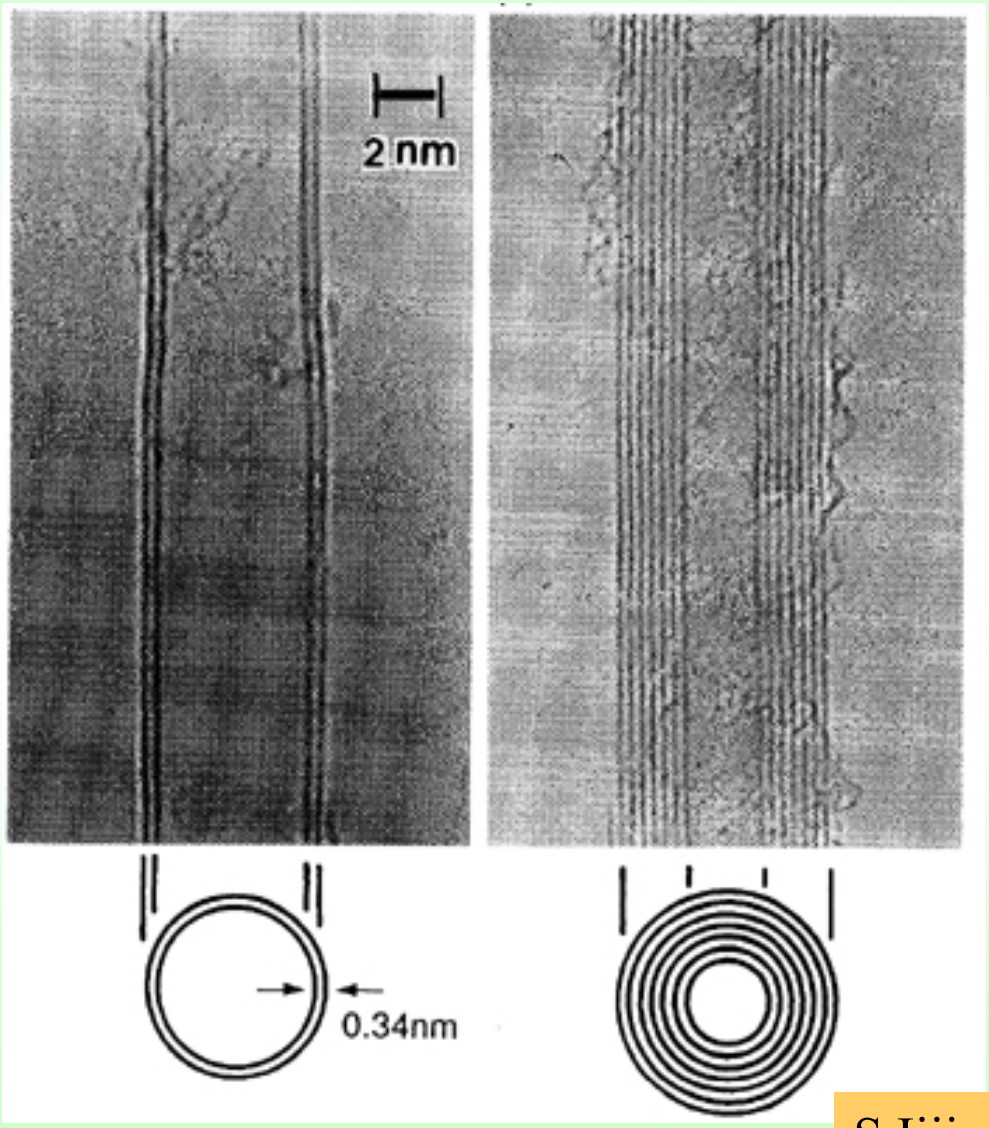
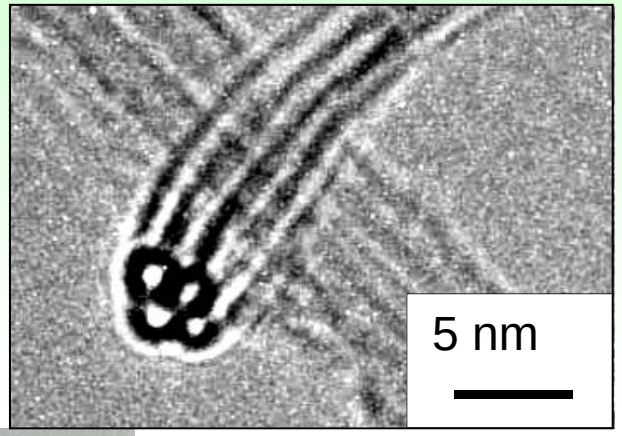
TEM Images of Carbon Nanotubes

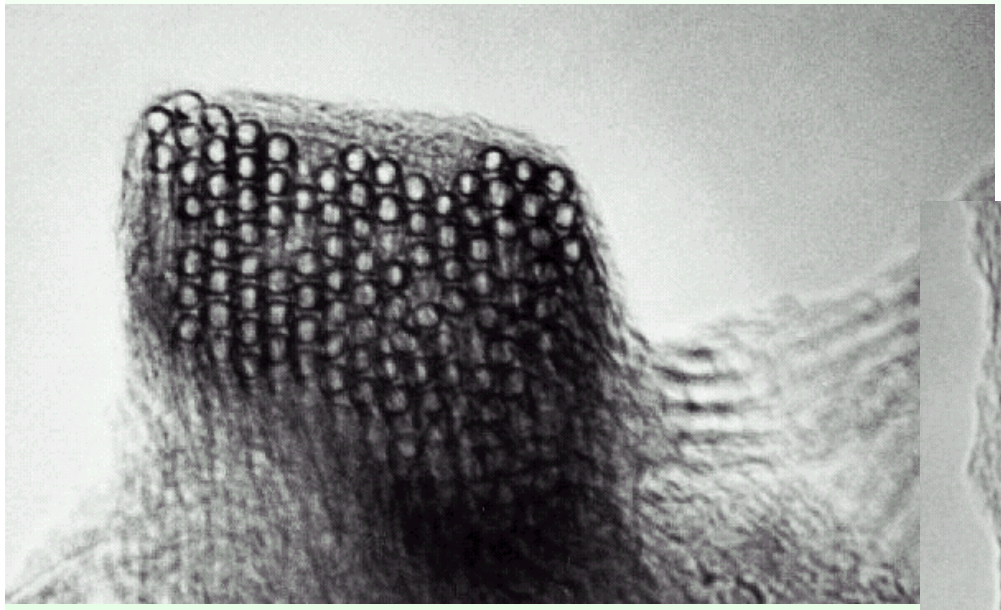


S.Iijima, Nature, 354, pp.56-58 (1991).

TEM Pictures of SWNT Ropes



By ACCVD

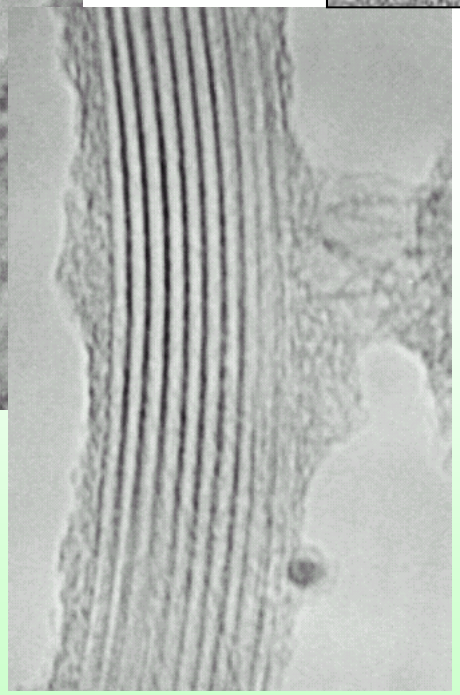


About 100 SWNTs

Individual tube diameter: 1.3 nm

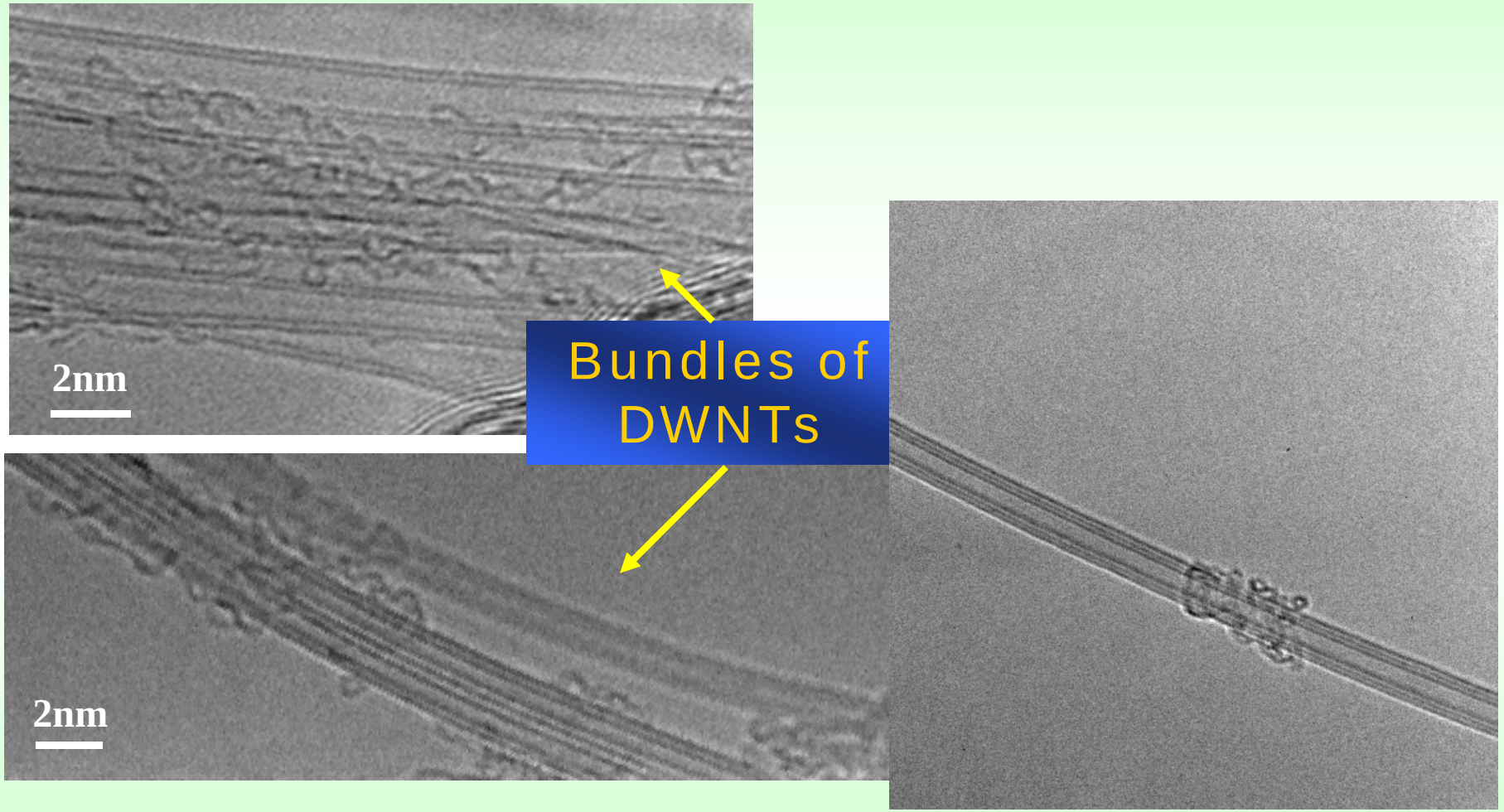
Spacing: 0.34 nm

Misalignments and Terminations



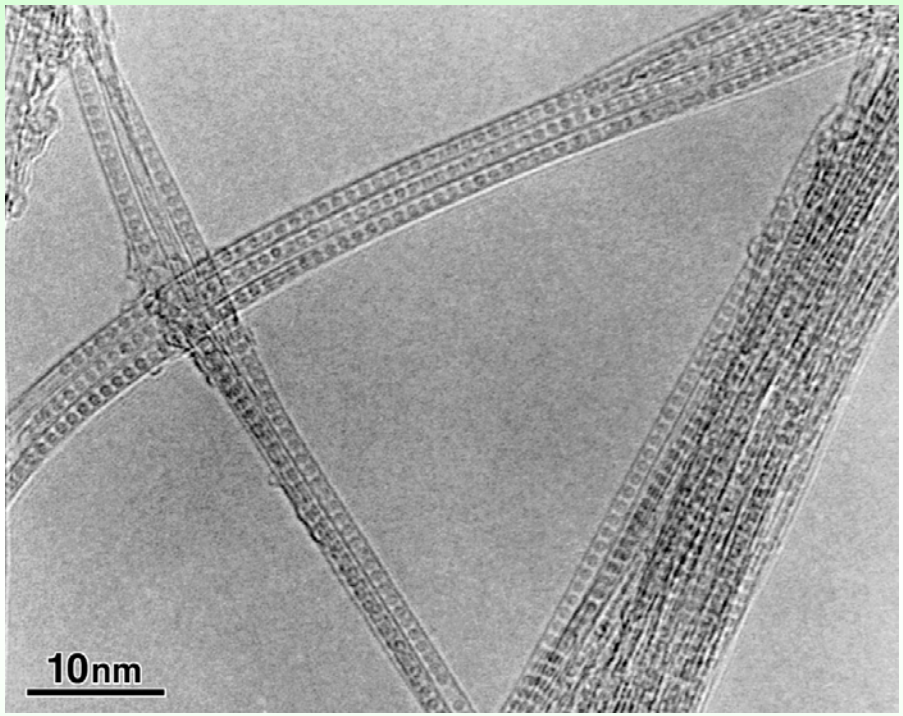
TEM from Smalley et al. at Rice University

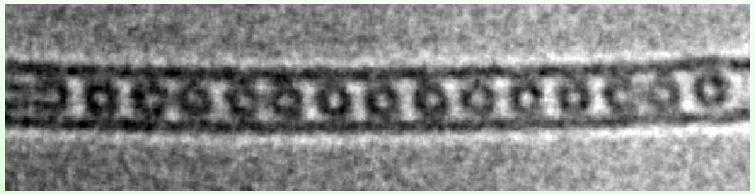
HRTEM images of DWNTs & TWNTs



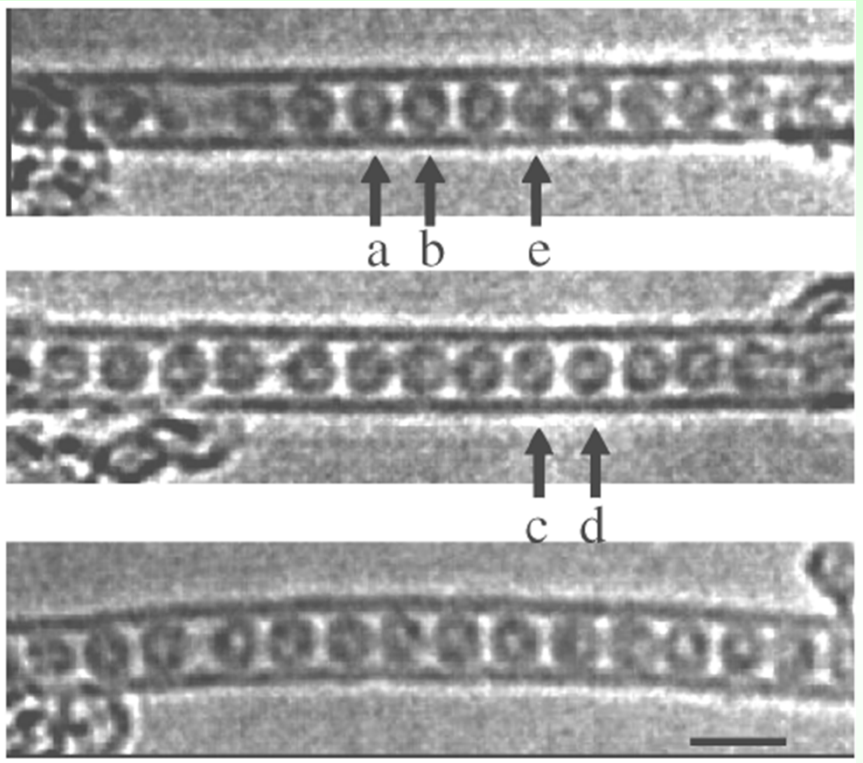
N. Shinohara's Powerpoint

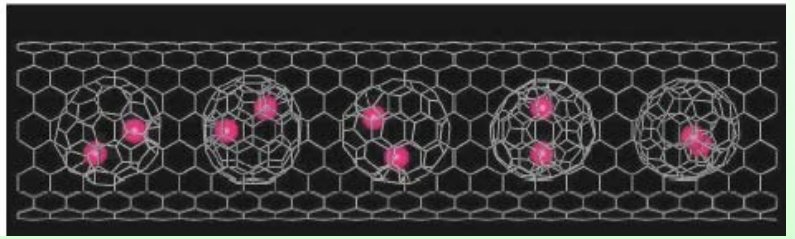
Peapods





Shinohara, 培風館



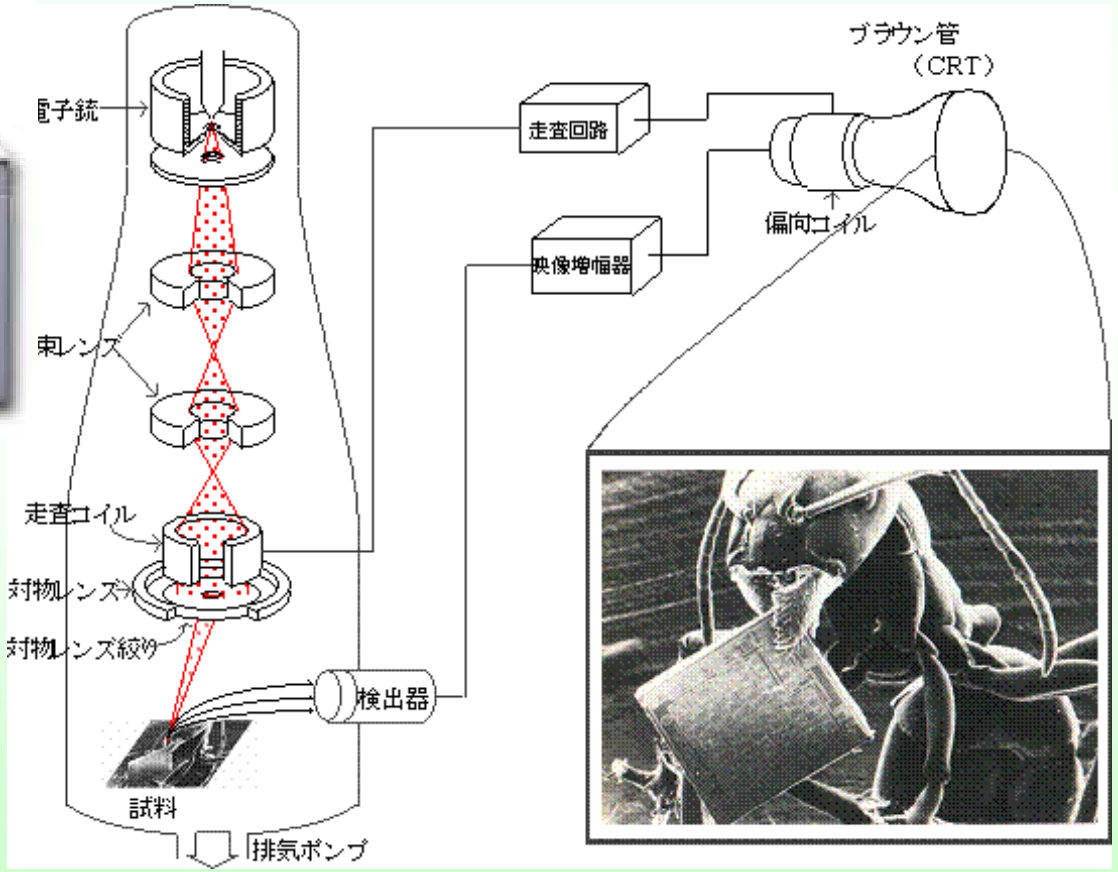


Peapod with $Sc_2@C_{84}$

Suenaga et al., PRL 2003

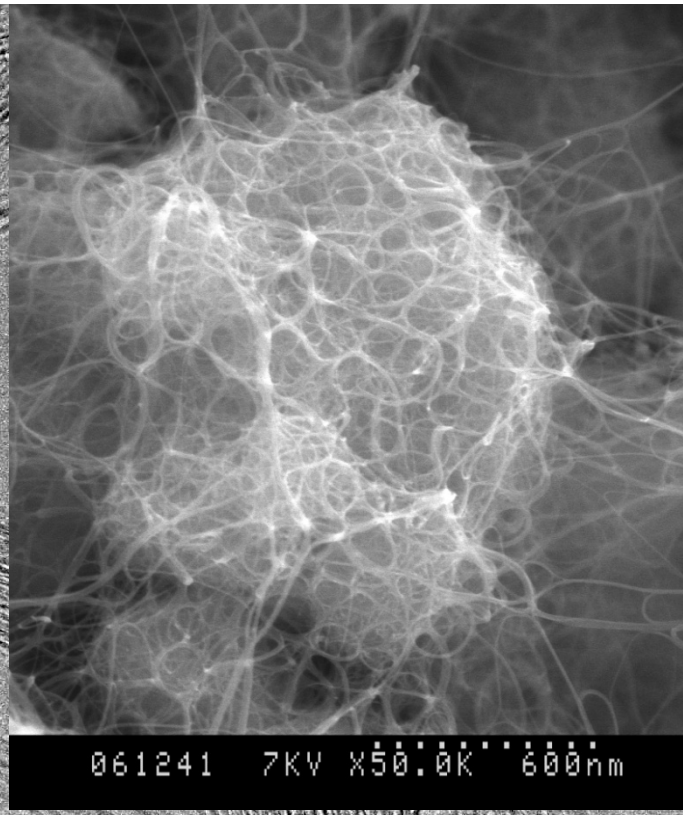
Scanning Electron Spectroscopy

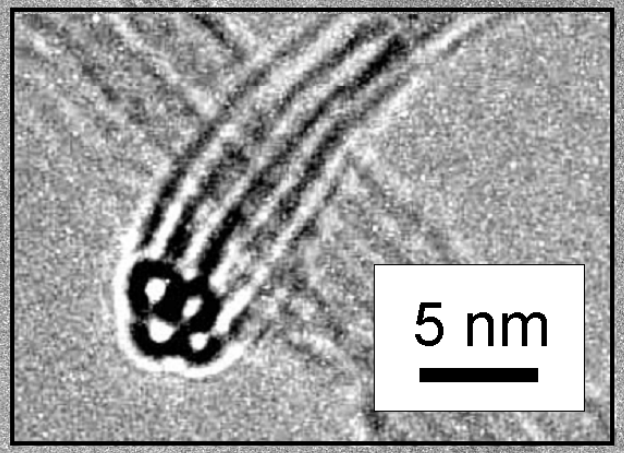
Hitachi S4800, 日立ハイテクHPより



http://www.remus.dti.ne.jp/~kkkkwing/

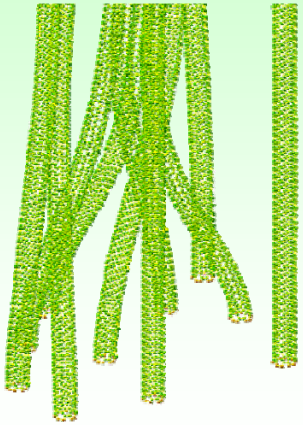
Images of As-Grown Sample

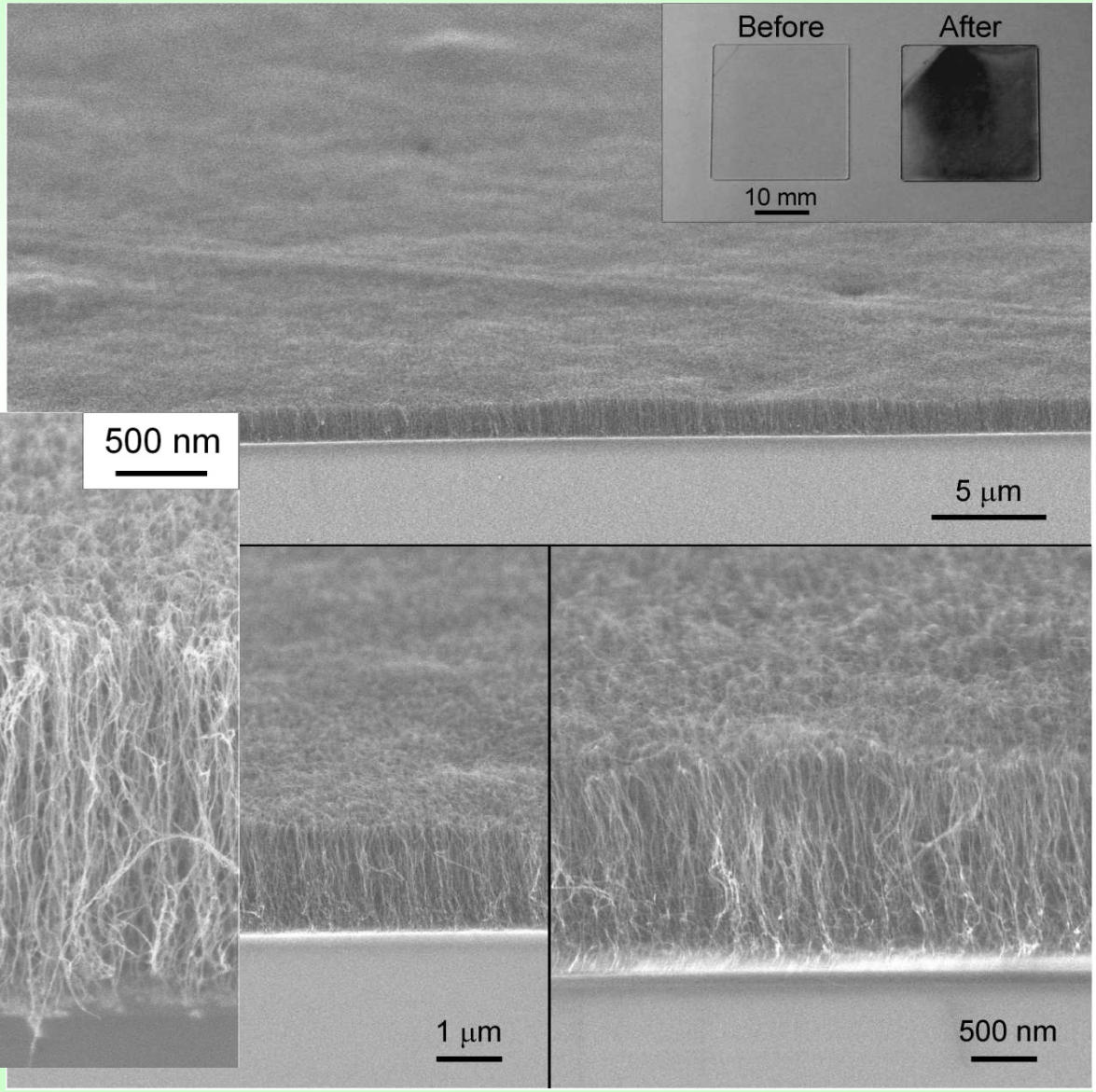




20 nm

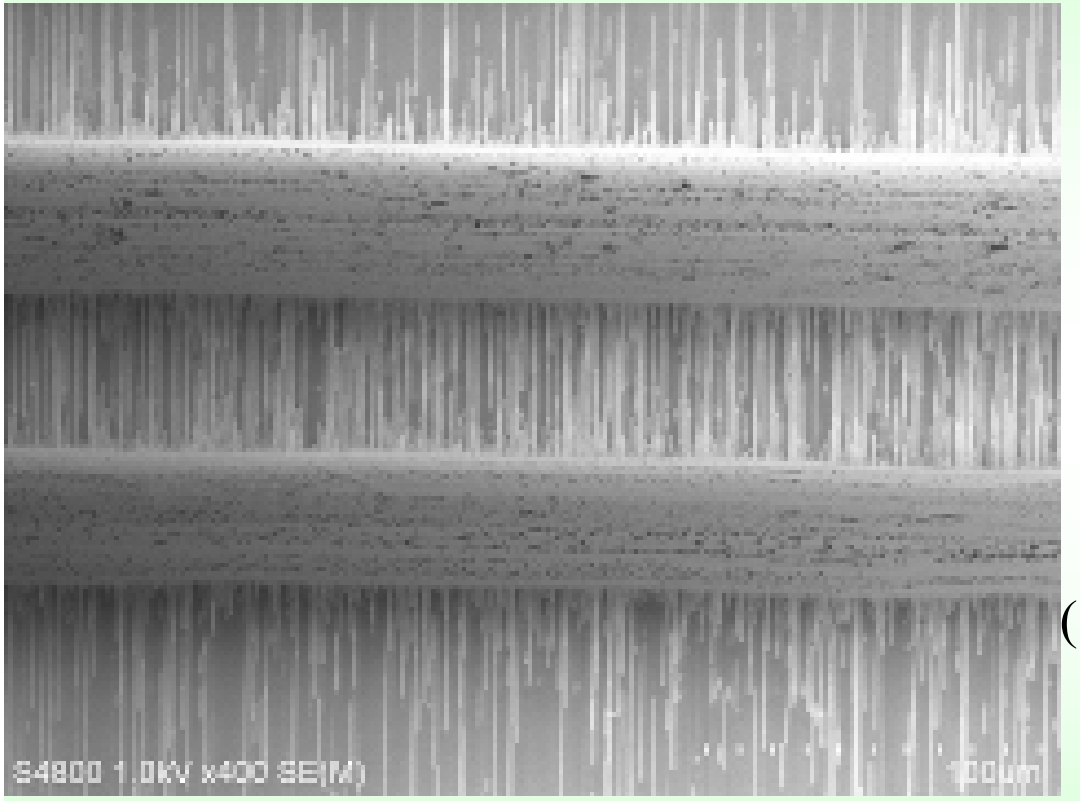
Vertically Aligned SWNTs on Quartz Substrate



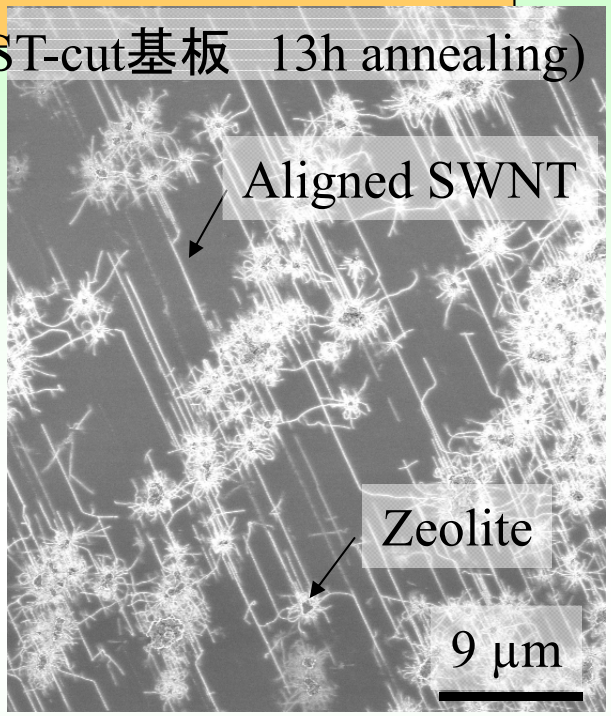


Y. Murakami, S. Chiashi, Y. Miyauchi, M. Hu, M. Ogura, T. Okubo, S. Maruyama, Chem. Phys. Lett. 385 (2004) 298

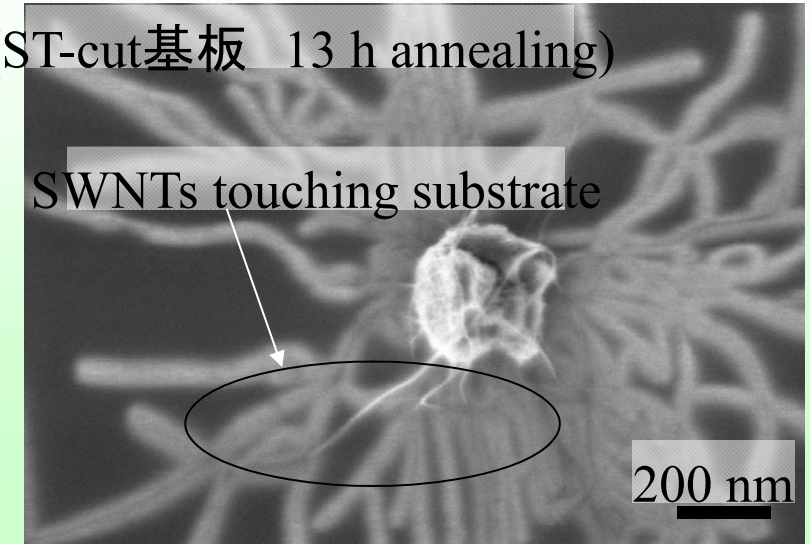
Horizontally Aligned SWNTs



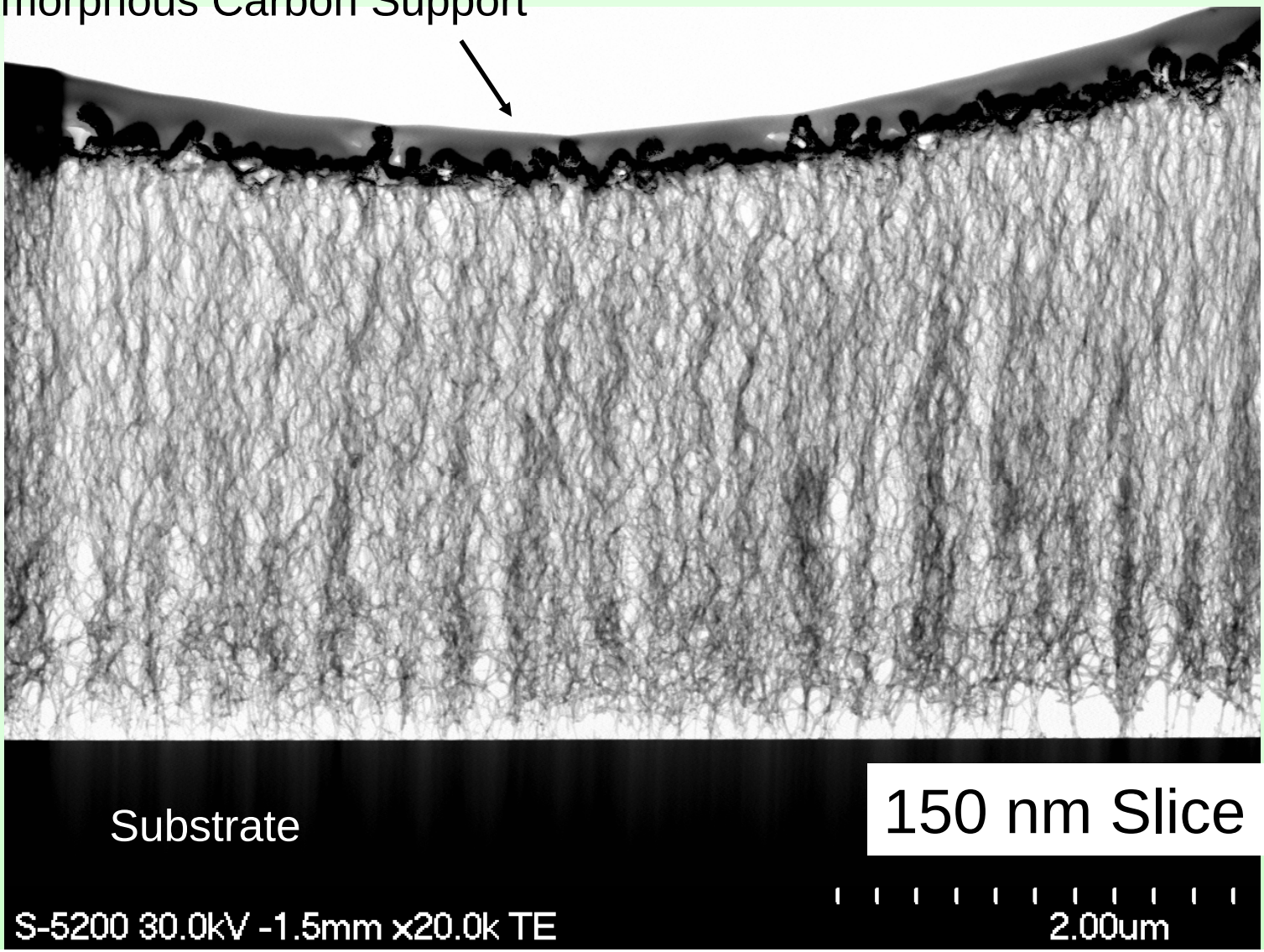
(ST-cut基板　13h annealing)



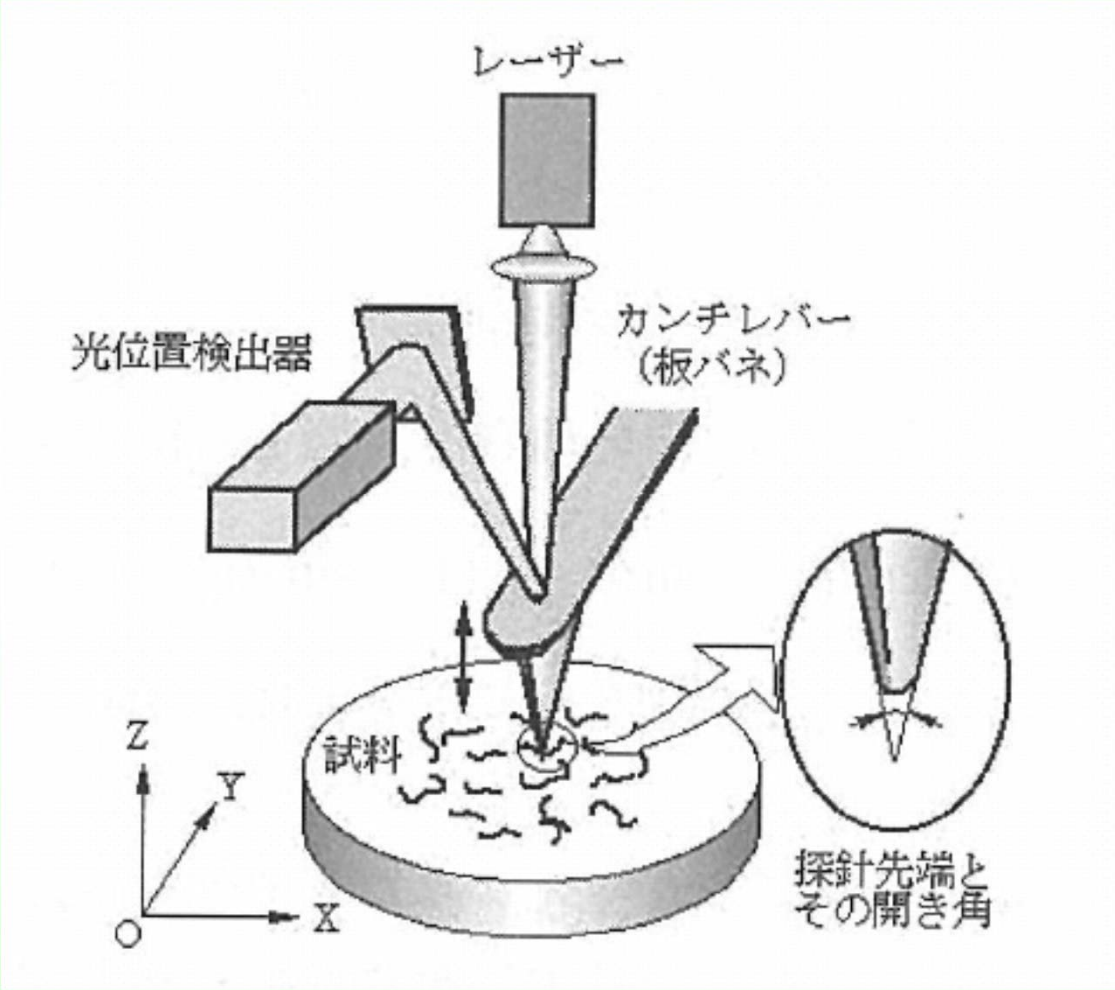
(ST-cut基板　13 h annealing)

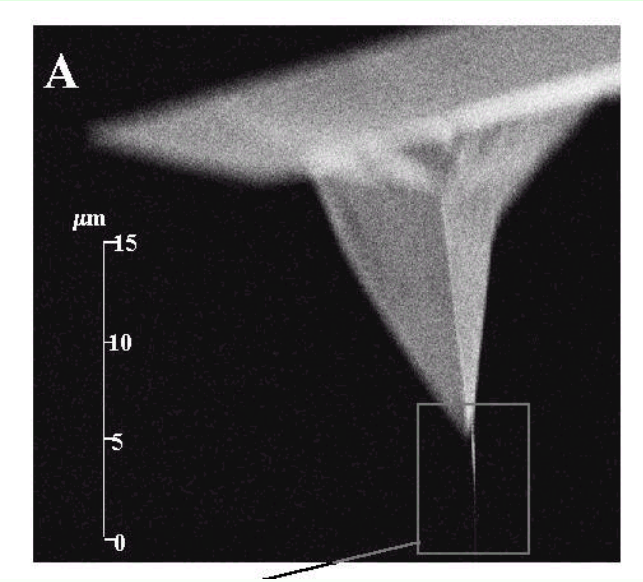


STEM Image of Vertically Aligned SWNTs



Scanning Probe Microscopy





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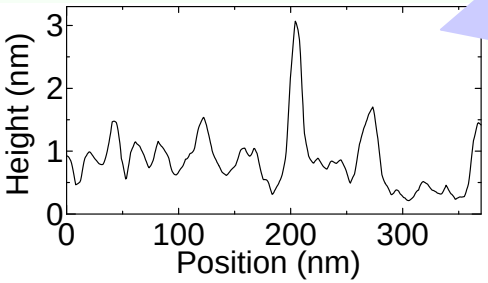
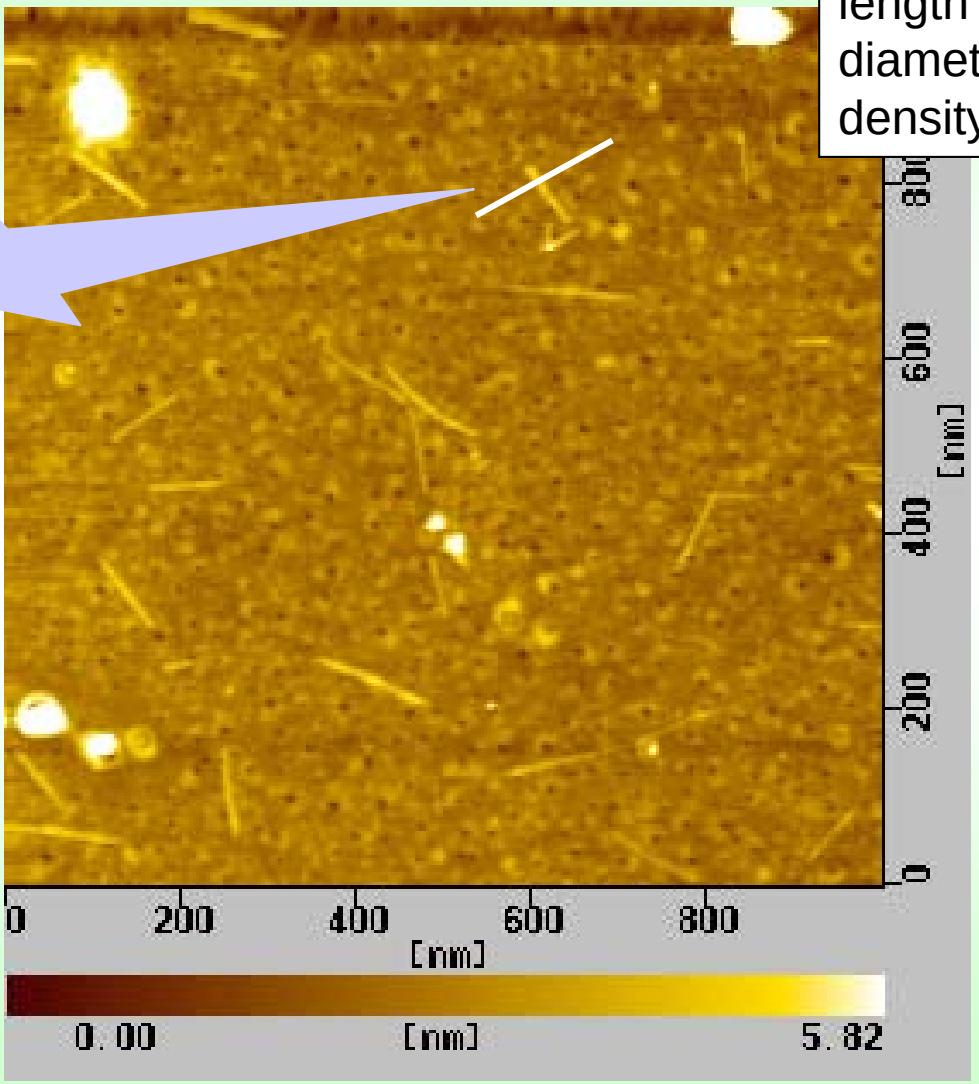
SWNTs Directly Generation on the AFM Stage

length : 100~150 nm
diameter : 1.3~2.2 nm
density : 10 μm^{-2}

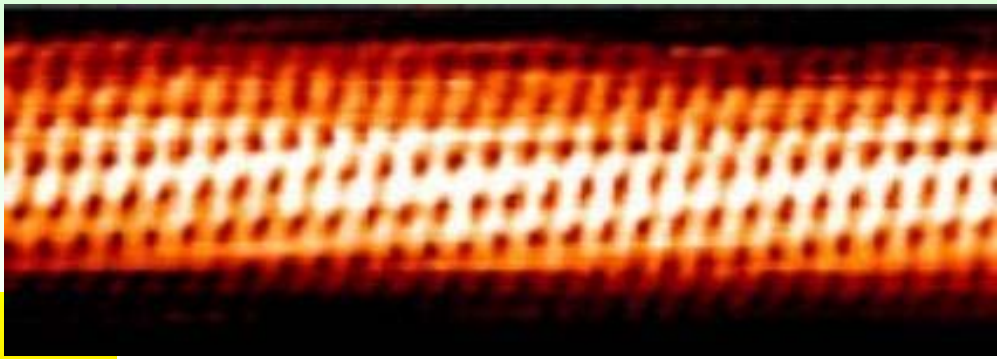
isolated SWNT
(not bundle)

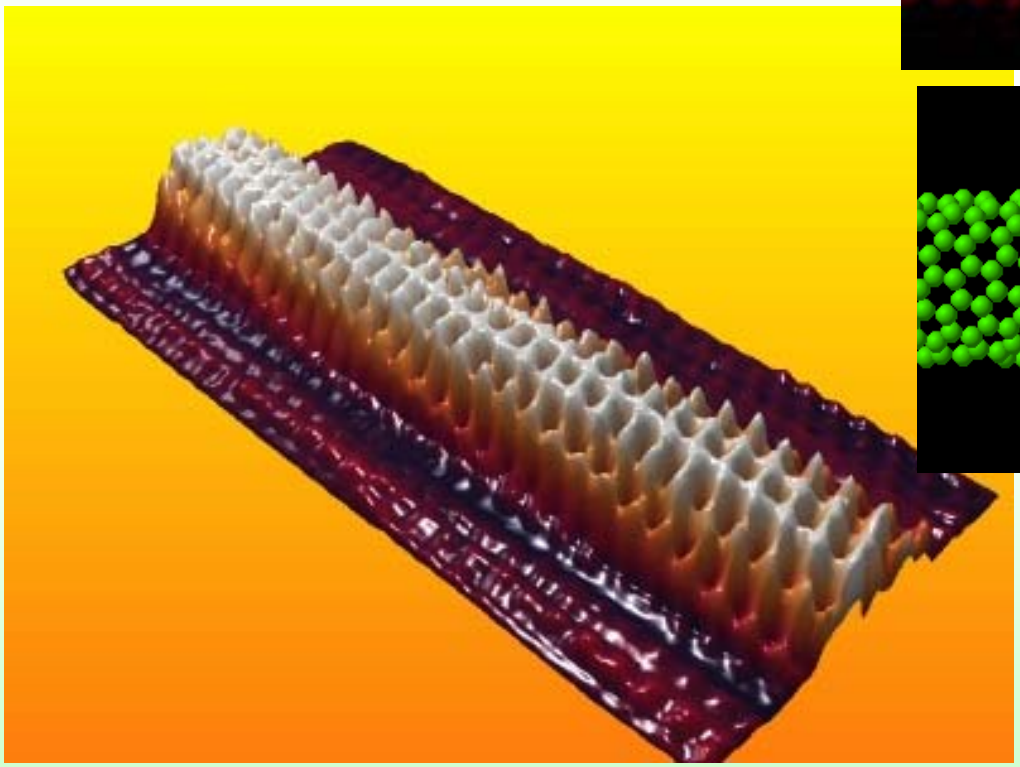


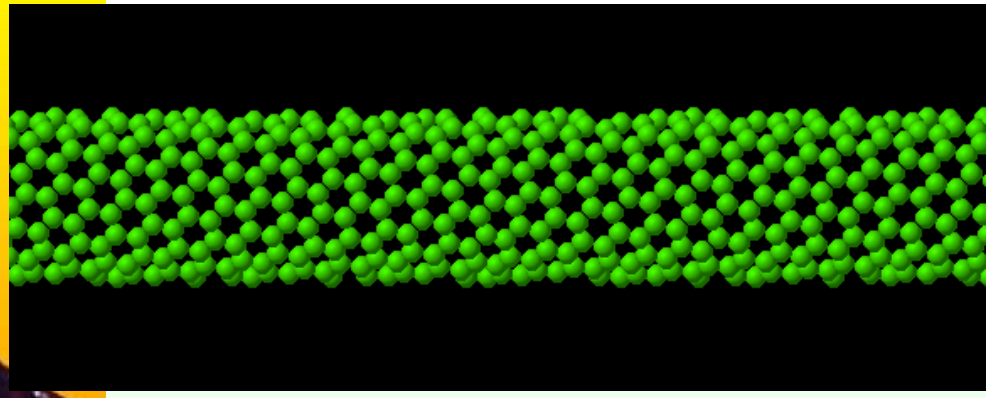


AFM image of SWNTs directly grown on silicon.

STM Image of Individual Atoms

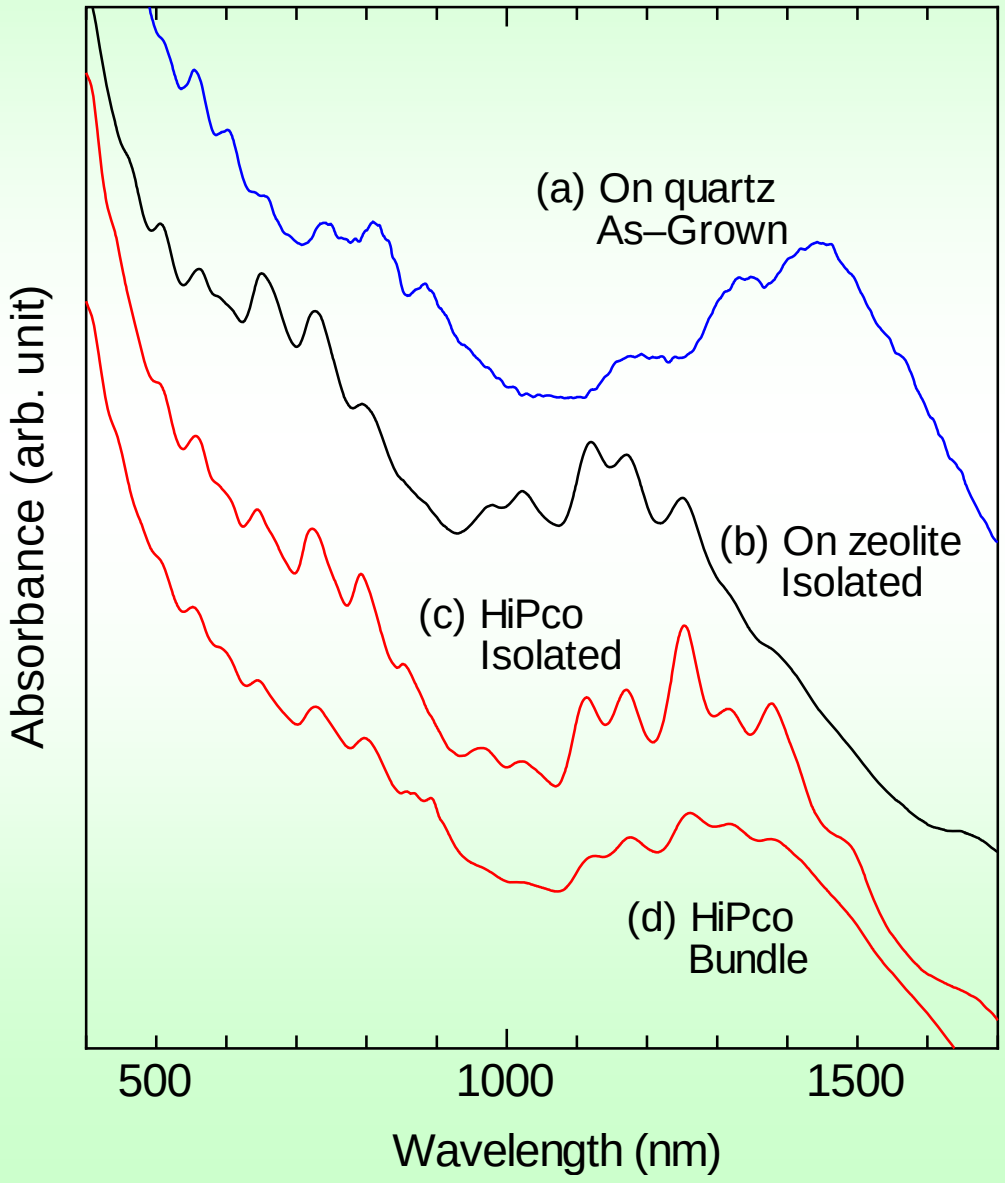


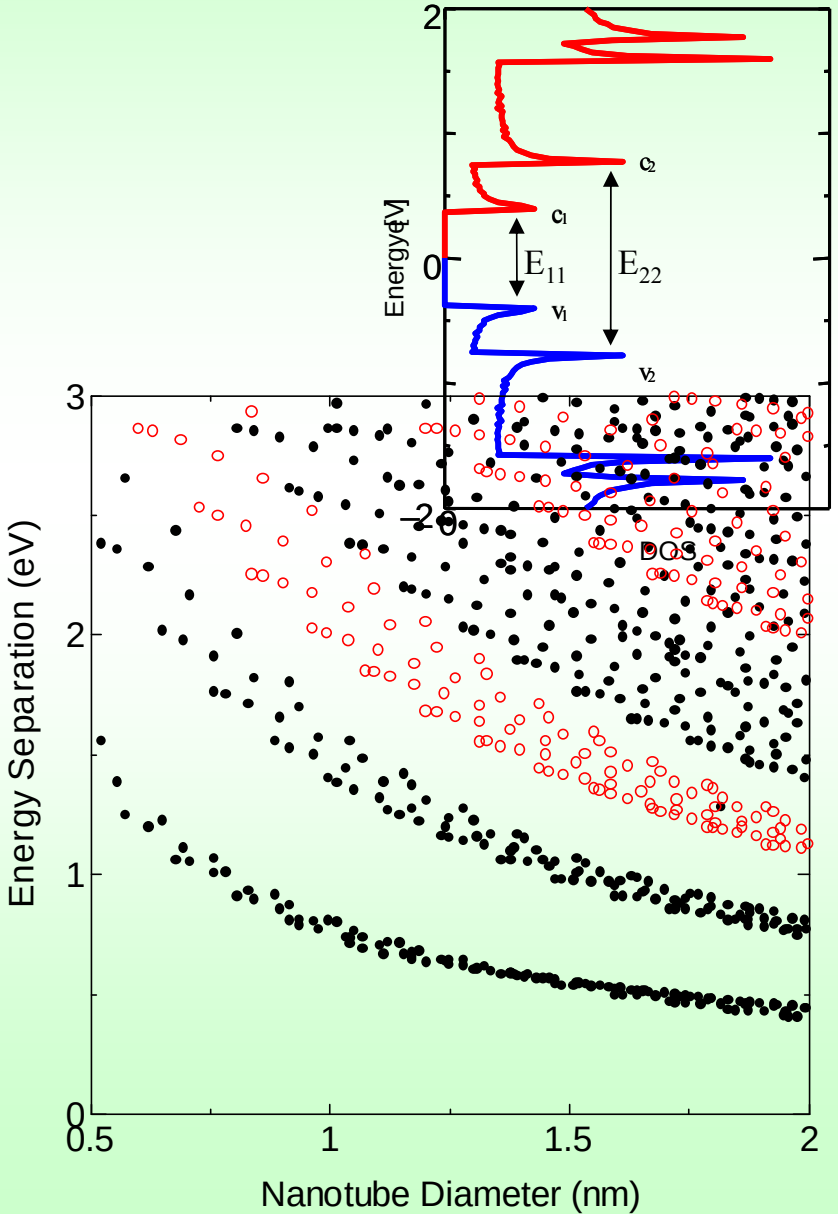




http://vortex.tn.tudelft.nl/~dekker/nanotubes.html

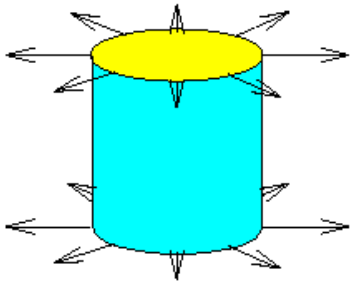
Absorption Spectra





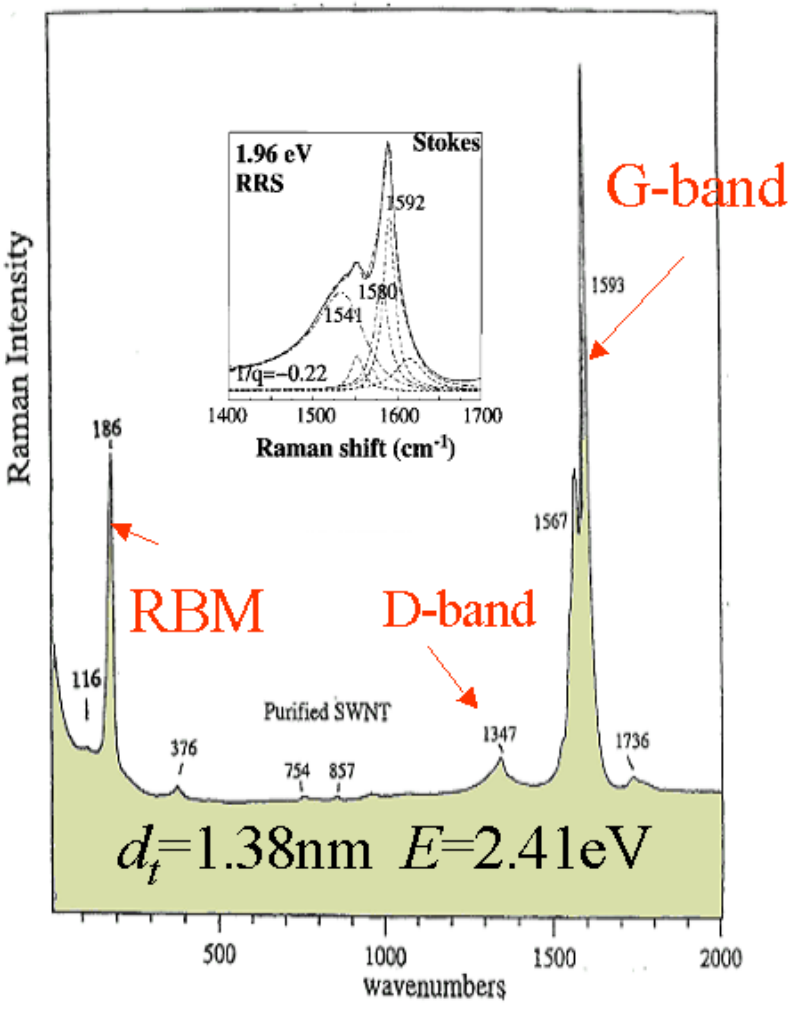
Resonance Raman Spectra of SWNTs

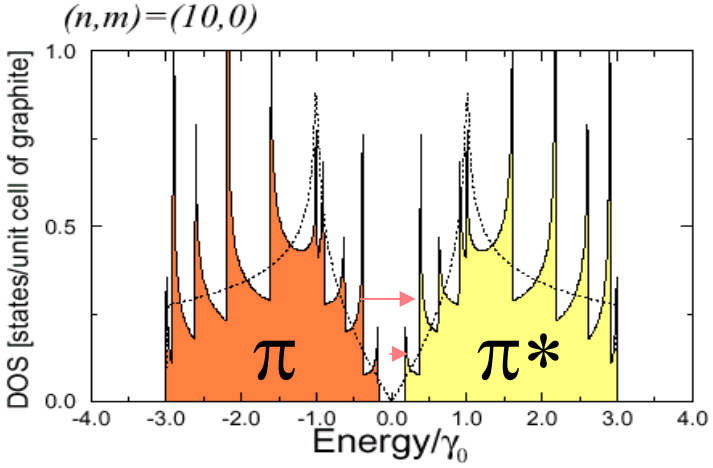
A.M. Rao et al, Science **275** (1997) 187



- RBM (Radial breathing Mode)
  - 100-400cm^{-1} $\prec d_t^{-1}$
- G-Band, (Graphite)
  - 1550-1600cm^{-1}, Splitting $\prec d_t^{-2}$
- BWF (Breit-Wigner-Fano) peaks $\prec d_t^{-1}$
  - 1520-1540cm^{-1}, Metallic SWNT
- **D-band, (Disorder)** depends on d_t
  - 1250-1350cm^{-1}, depends on E_{laser}

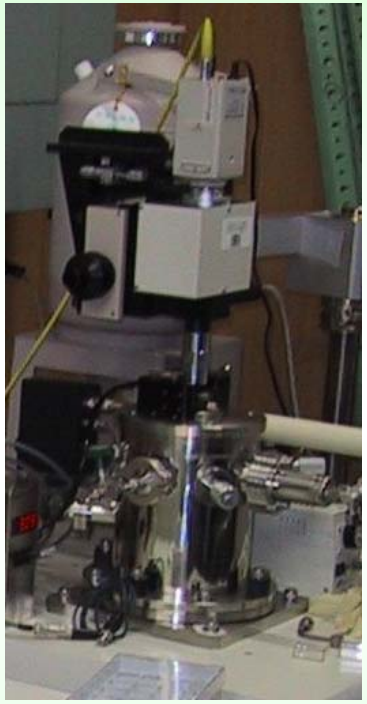
Diameter Selective



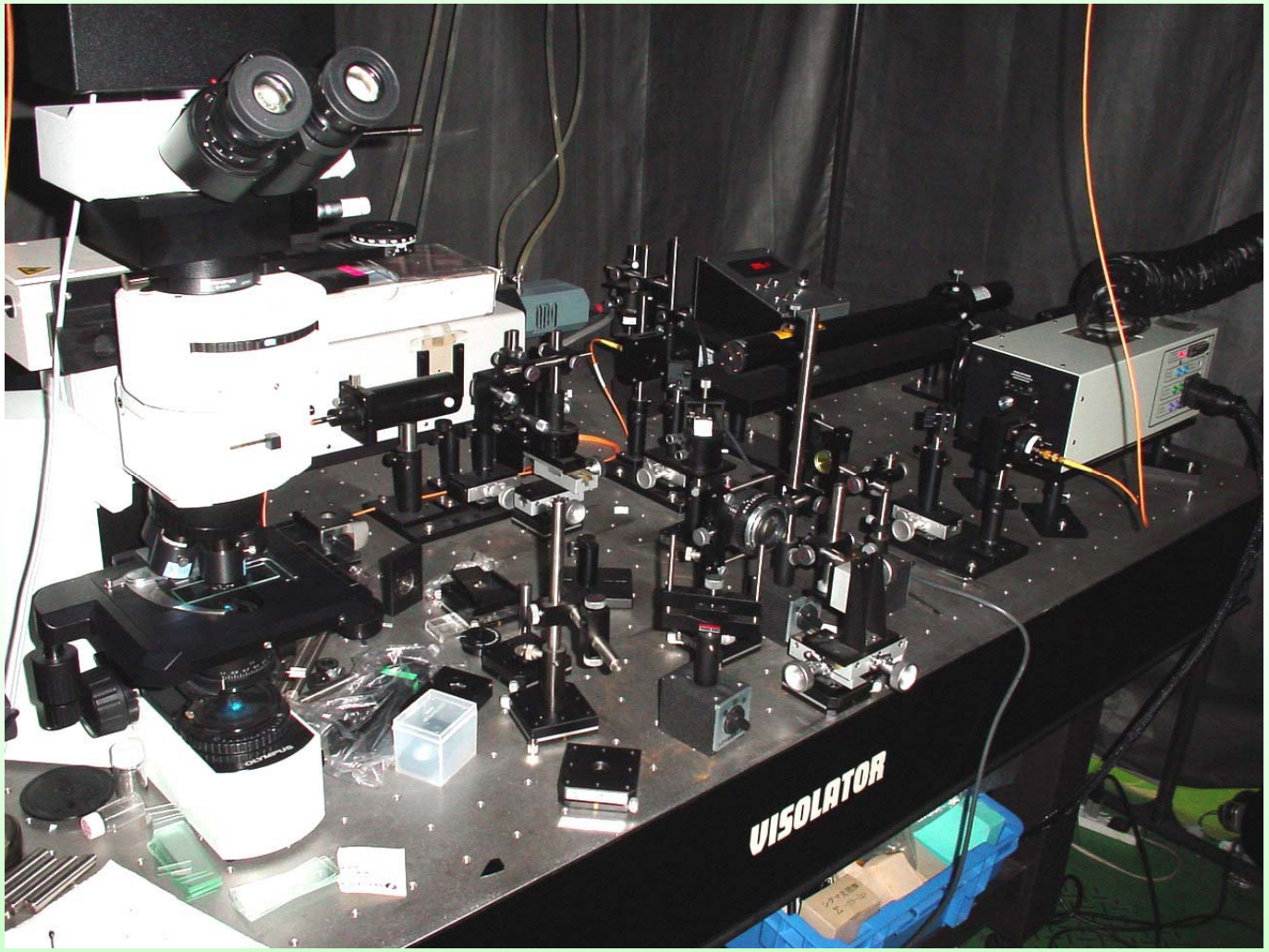


Electronic density of states

Raman Spectrometer

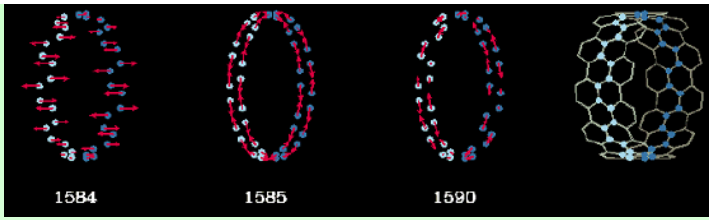


AFM/STM

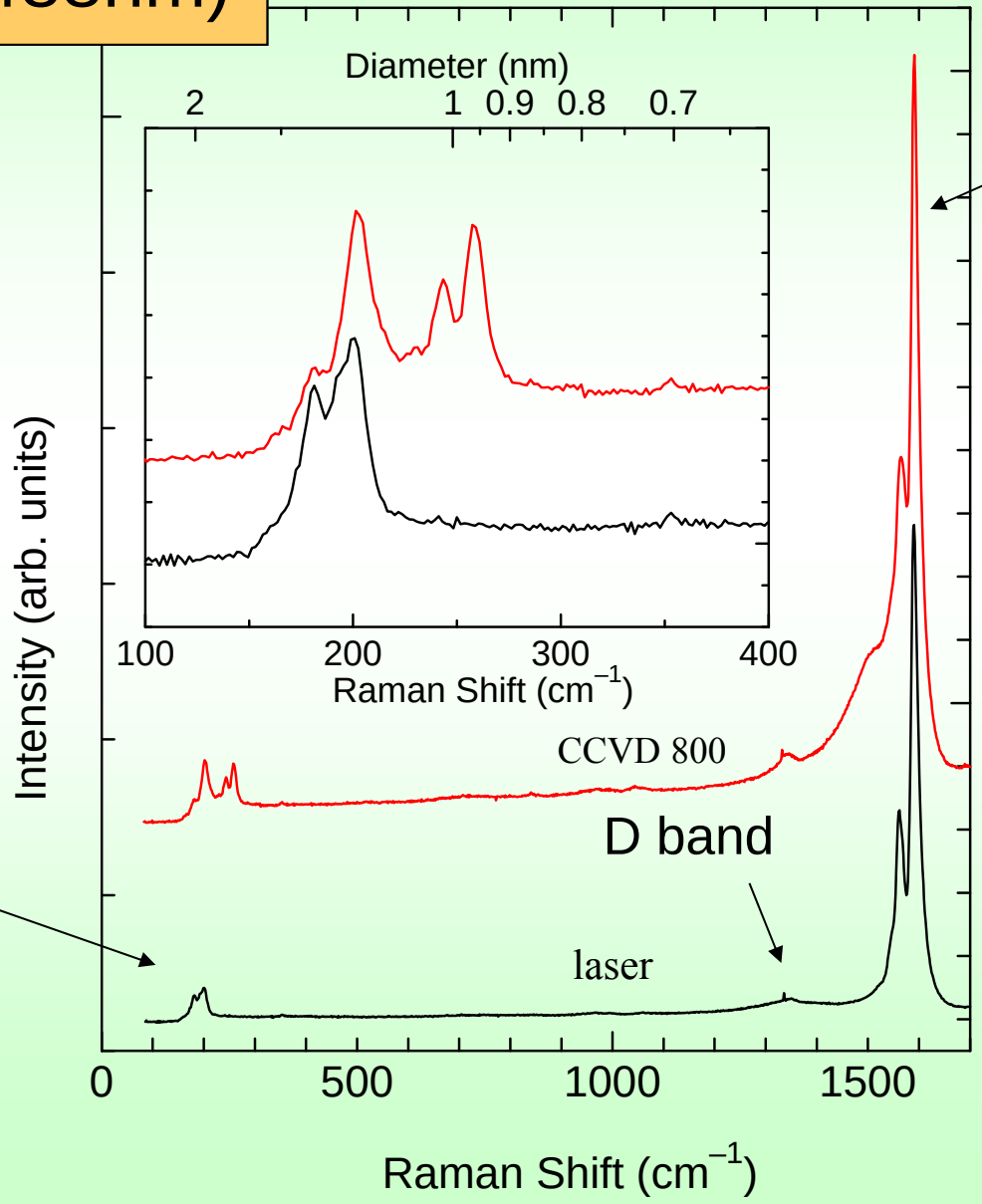


Micro and Macro Raman

Raman Scattering (Excitation 488nm)

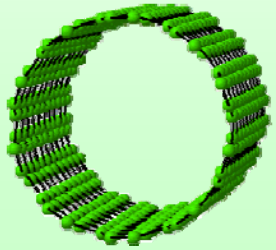


$$d\,(nm) = \frac{248}{\omega\,(cm^{-1})}$$

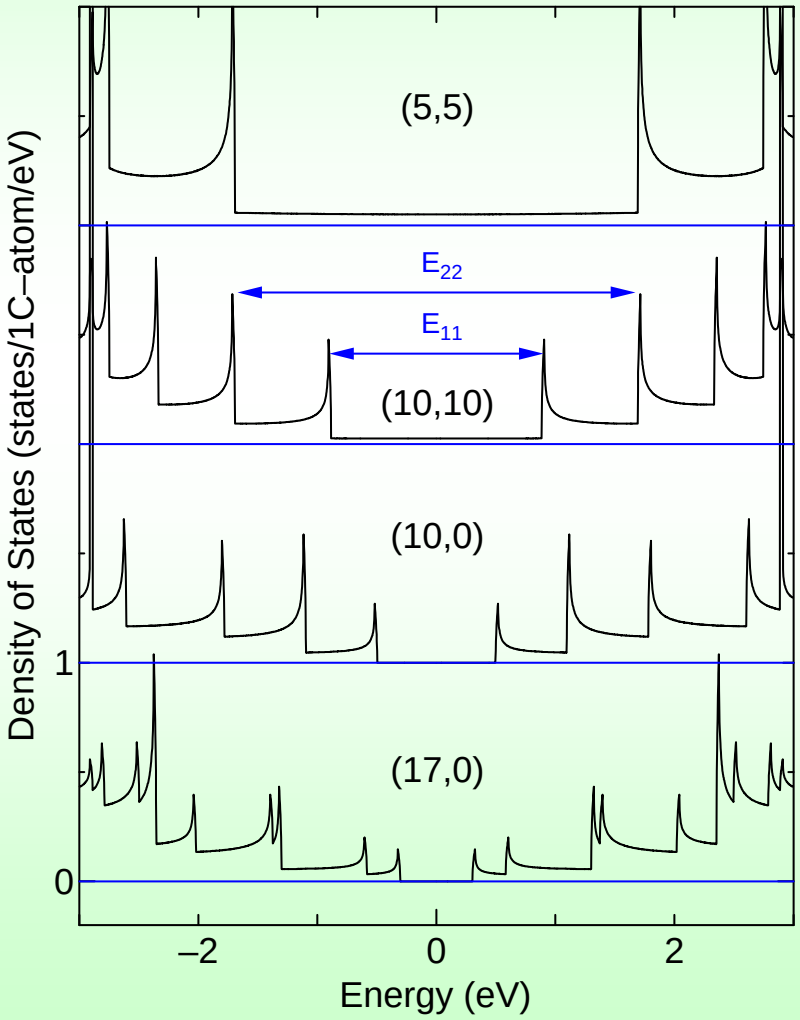


G band (Tangential Mode)

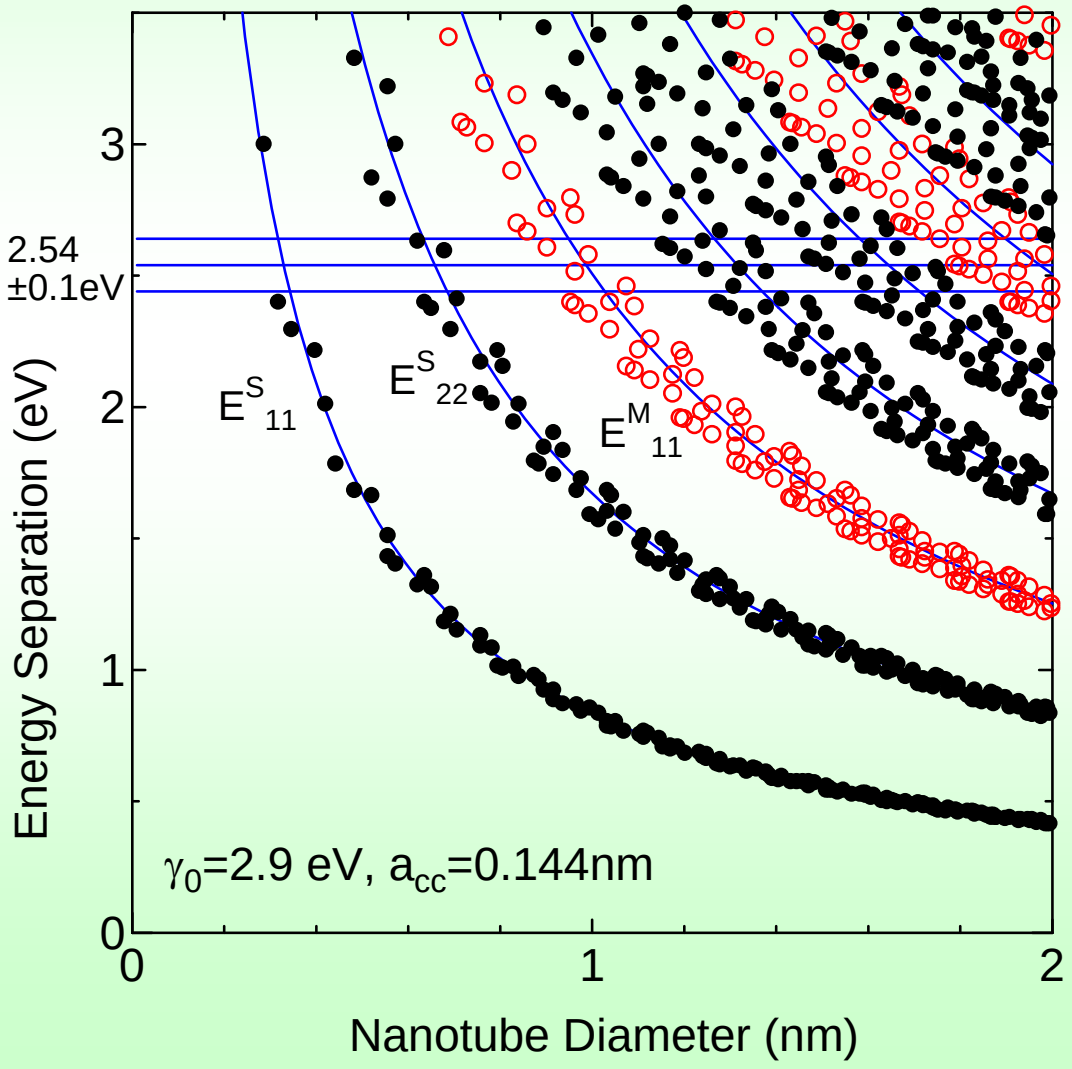
Radial Breathing Mode (RBM)



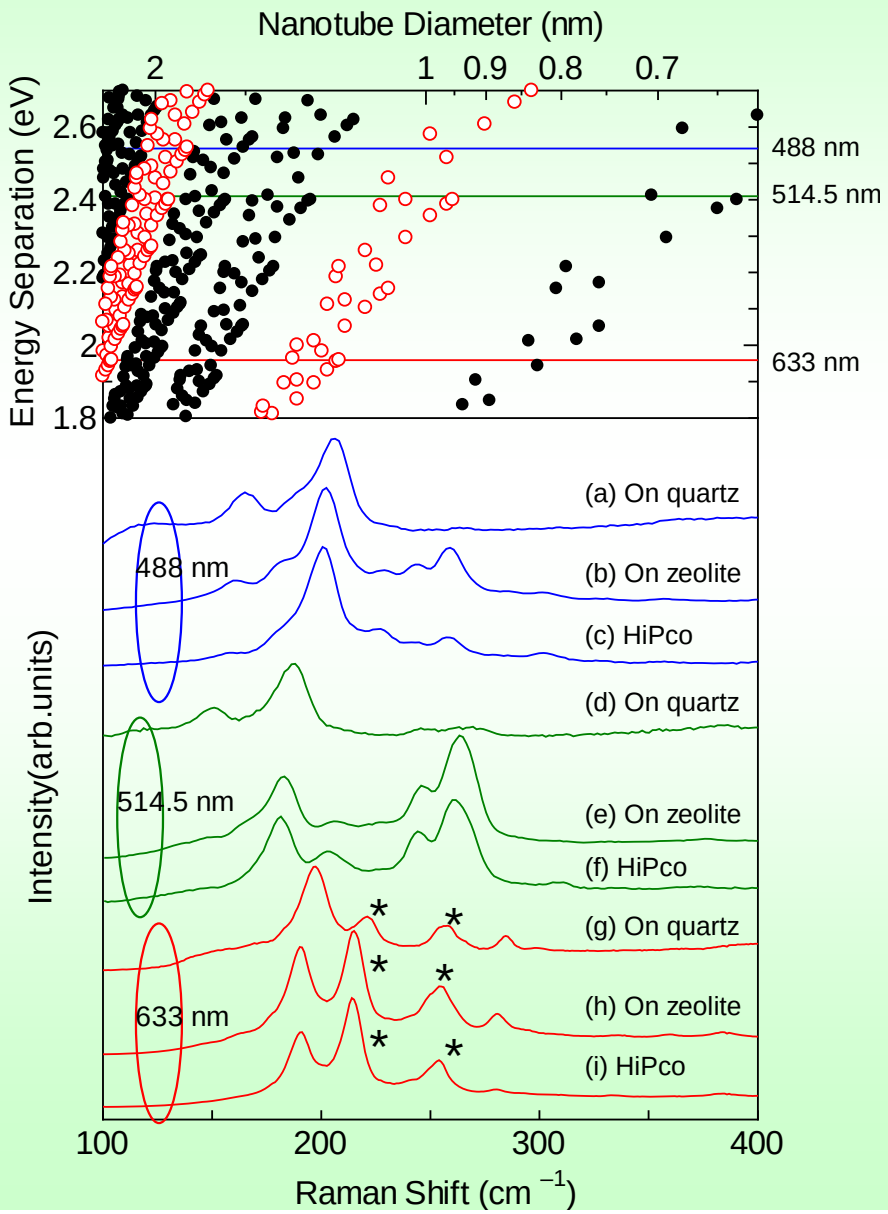
Kataura Plot

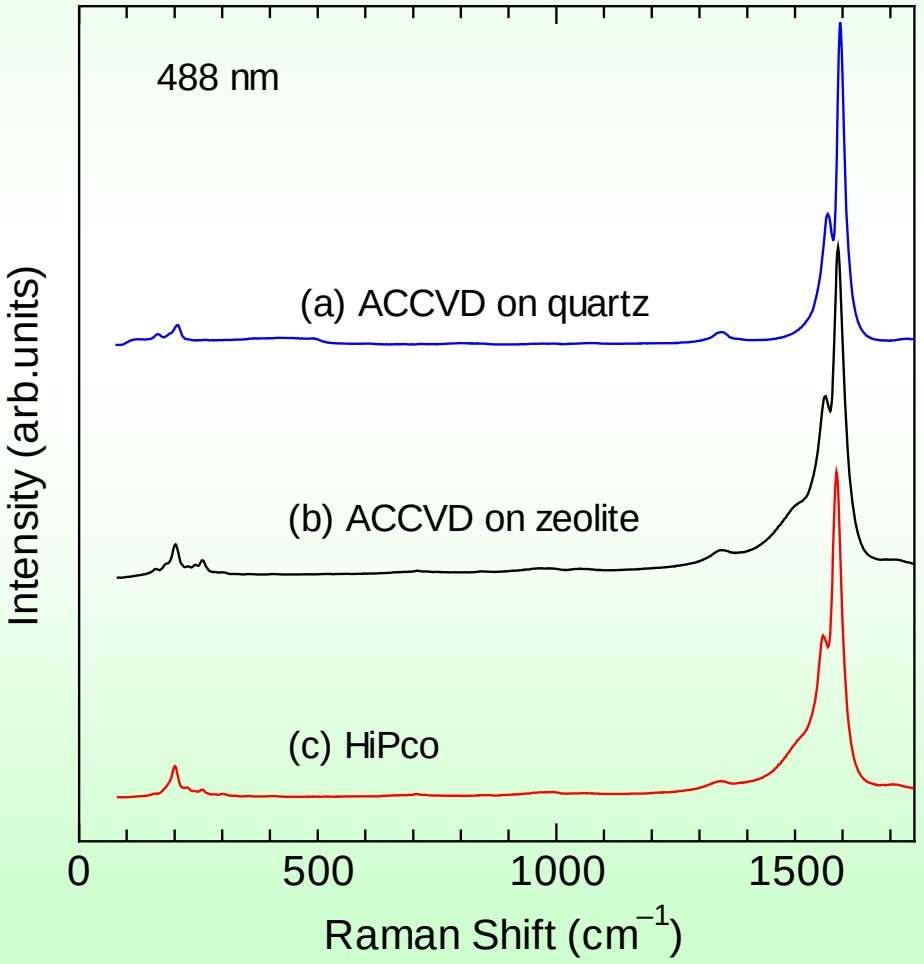


$E^{M}{}_{11}(d_t) = 6a_{cc}\gamma_0 / d_t$ $E^{S}{}_{11}(d_t) = 2a_{cc}\gamma_0 / d_t$

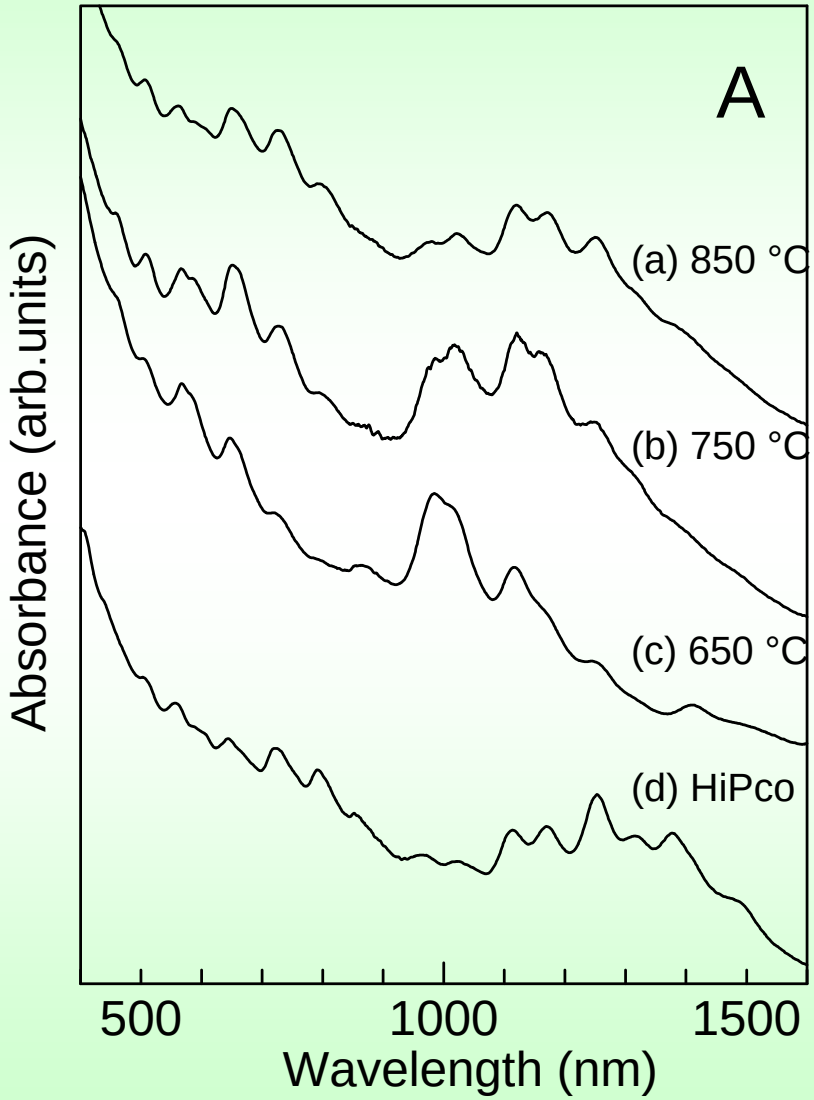


Raman Spectra

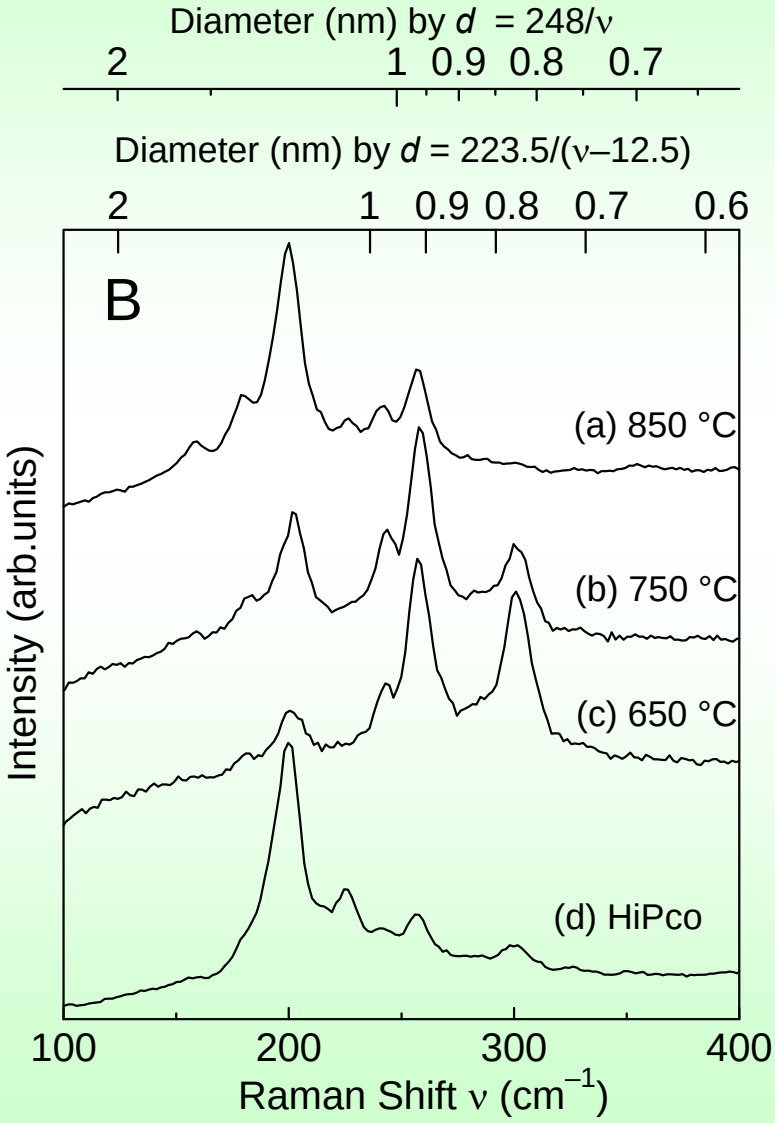




Optical absorption and Raman RBM

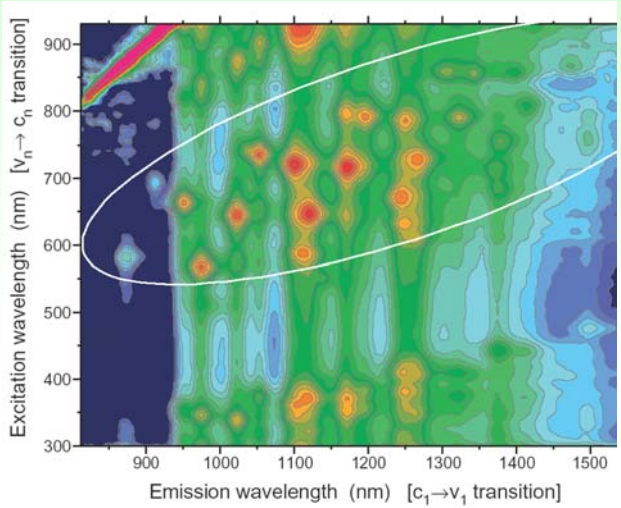


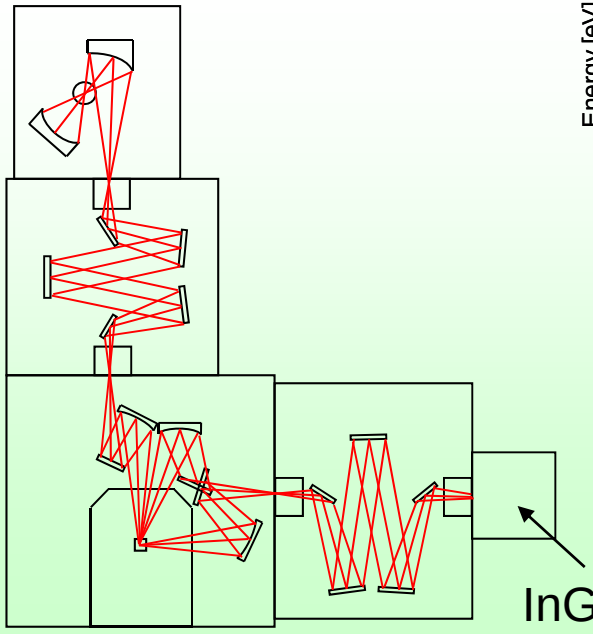
Absorption of Isolated SWNTs



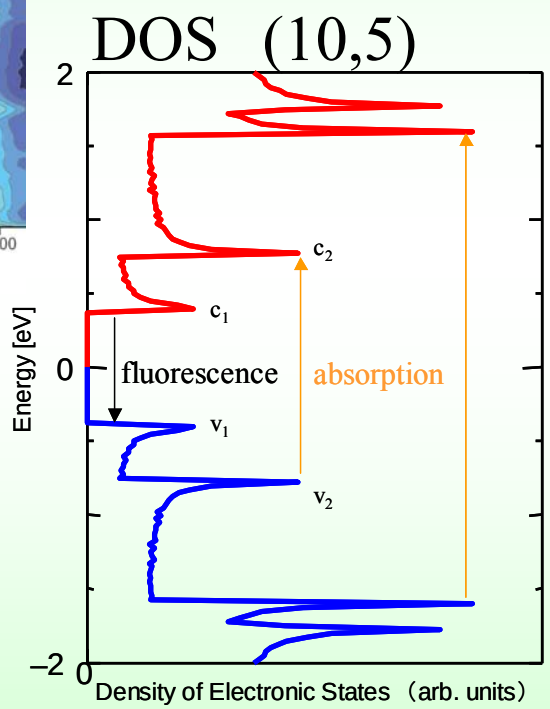
Raman RBM of ‘as grown’ samples

Band Gap Fluorescence

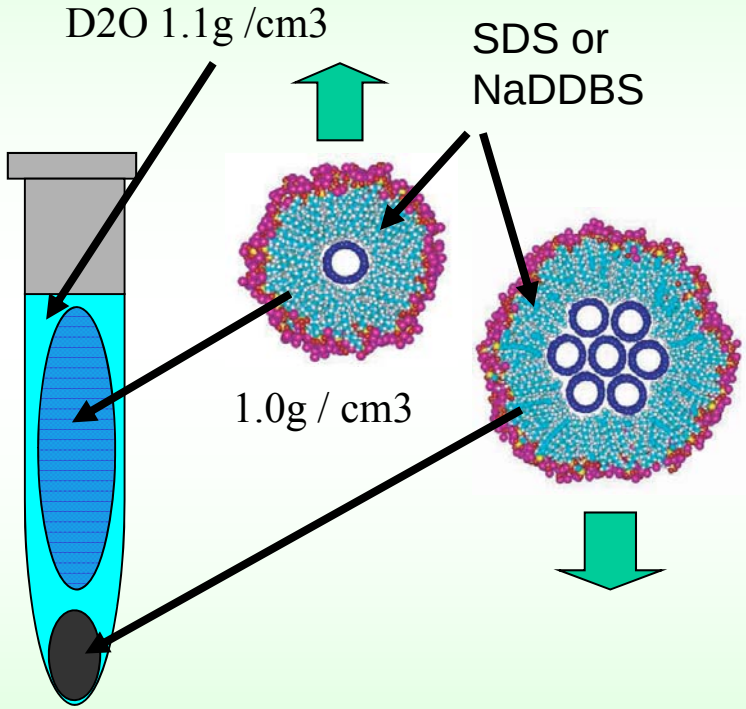




InGaAs Detector



Strong Sonication 60min



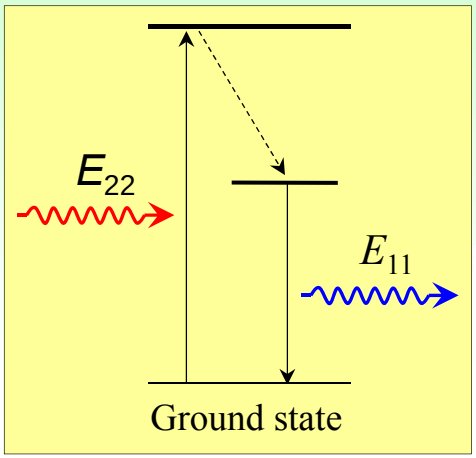
Centrifugation 20,627g x 24h

Centrifugation 180,000g x 1h

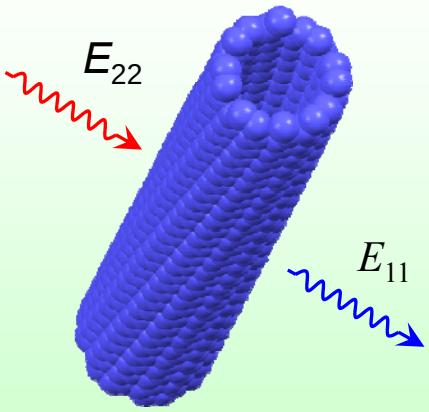
M. J. O'Connell et al., Science 297 (2002) 593

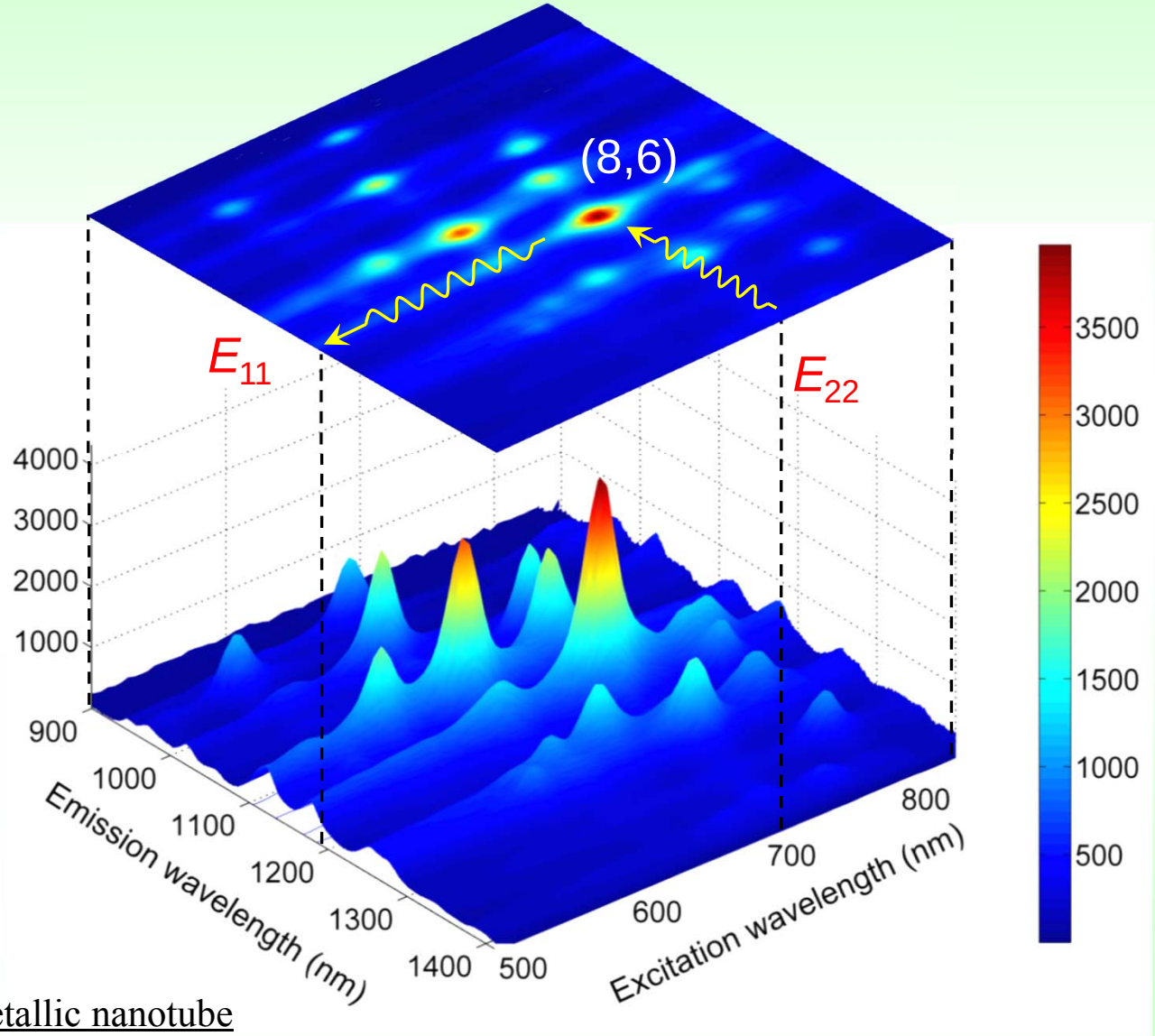
S. M. Bachilo *et al.,* Science 298 (2002) 2361.

Photoluminescence (PL) excitation spectroscopy



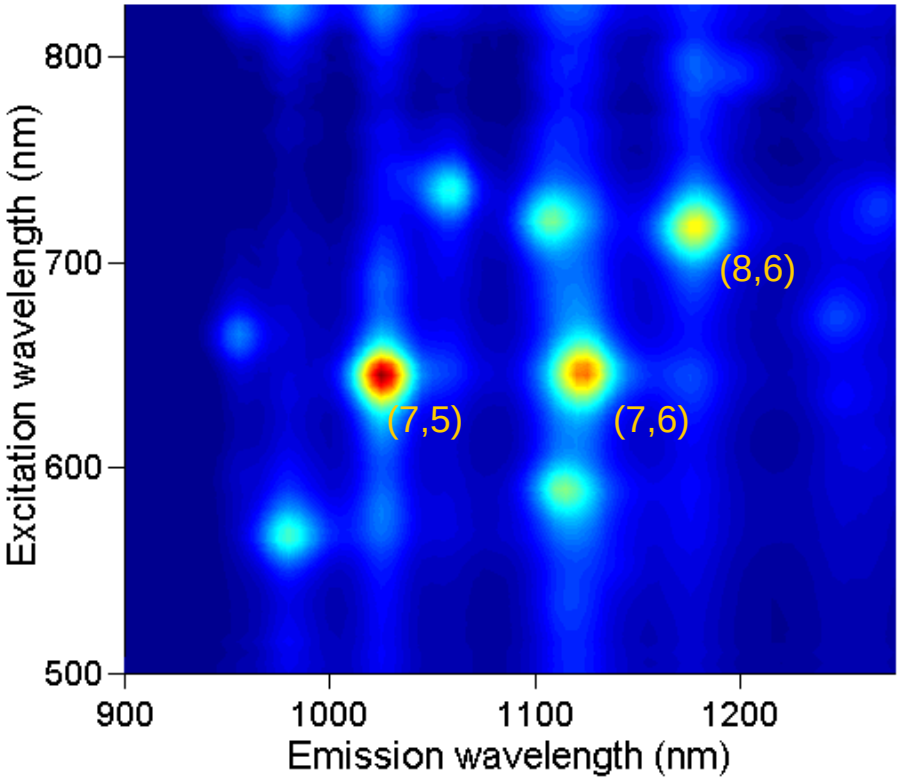
(8,6) SWNT



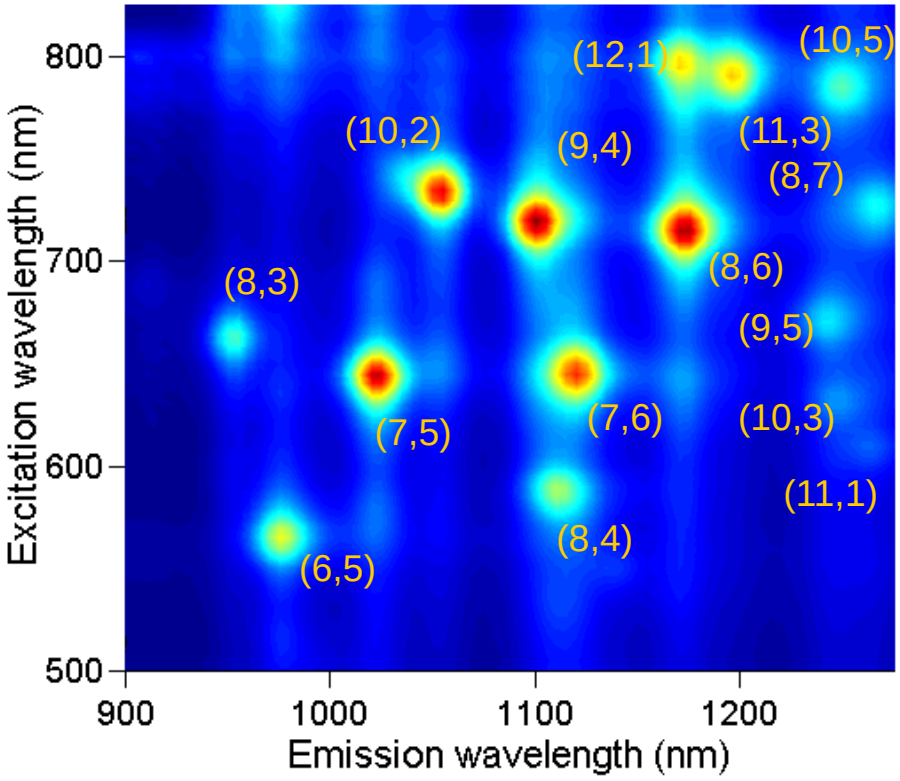


*** No fluorescence in <u>metallic nanotube</u>

Comparison of ACCVD and HiPco

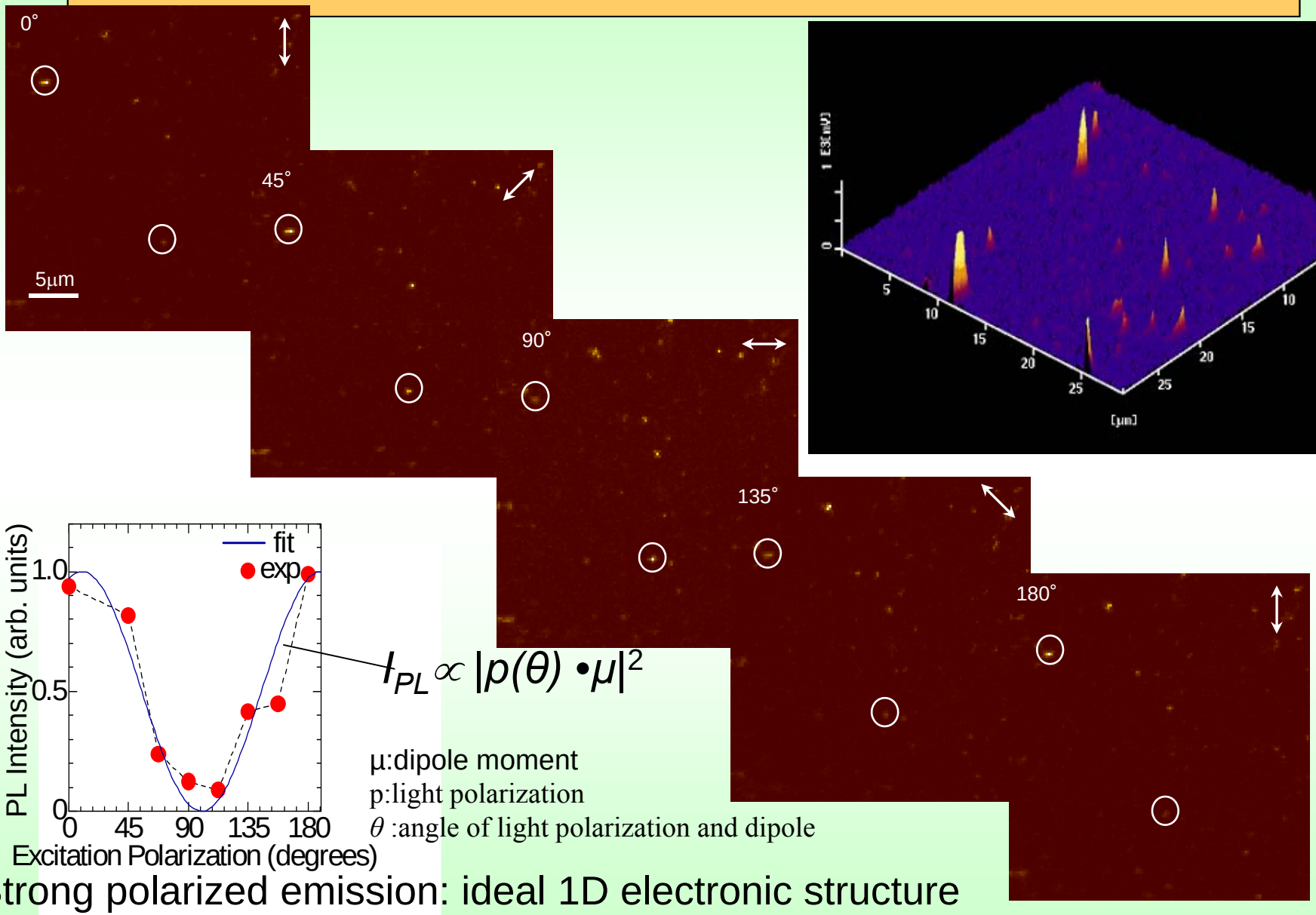


(a) ACCVD 850℃



(b) HiPco

Photoluminescence from Individual Nanotube



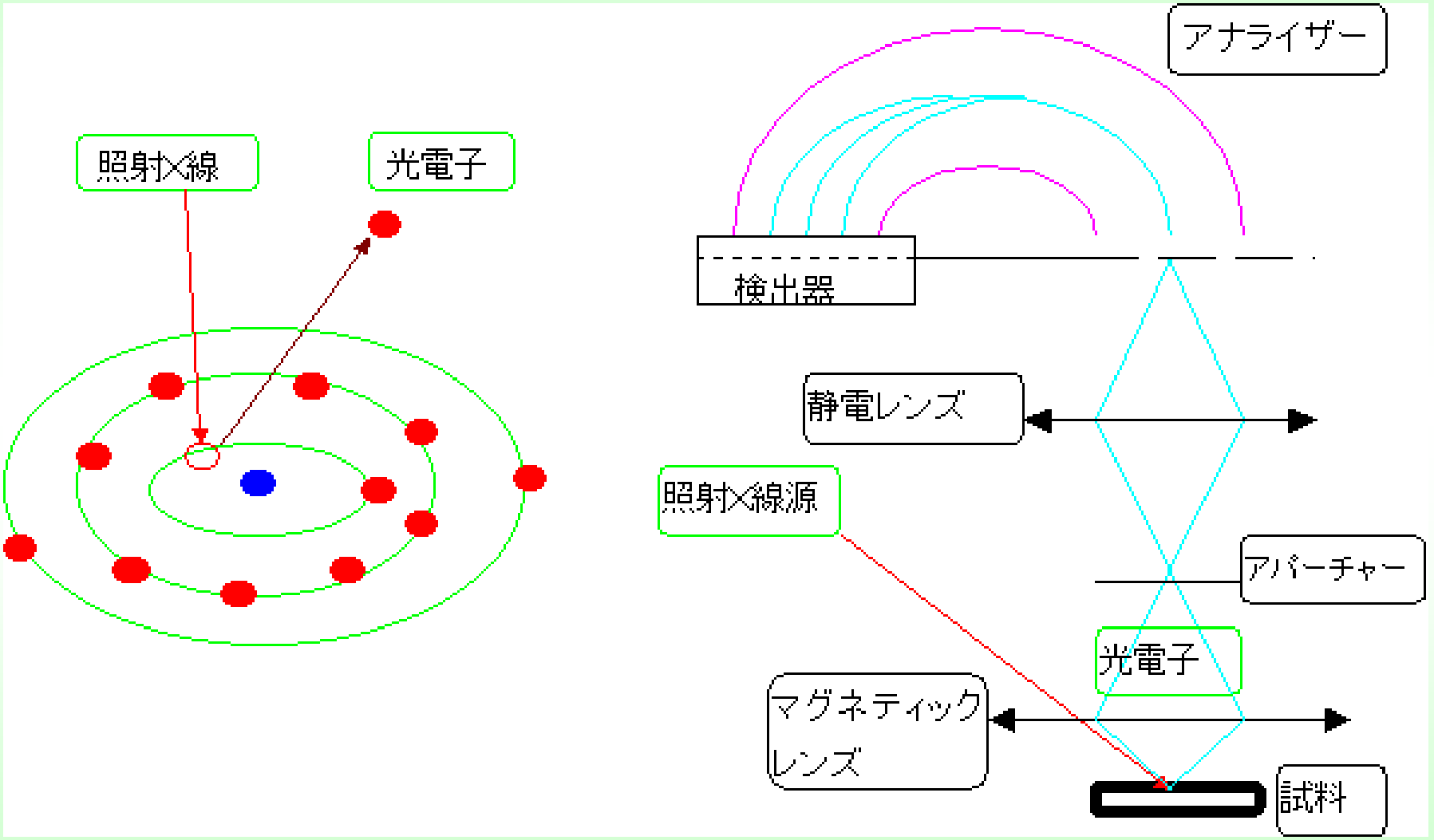
$$I_{PL} \propto |p(\theta) \bullet \mu|^2$$

μ:dipole moment
p:light polarization
θ :angle of light polarization and dipole

Strong polarized emission: ideal 1D electronic structure

Collaboration with K. Matsuda (KAST, Saeki Group) (2004)

XPS

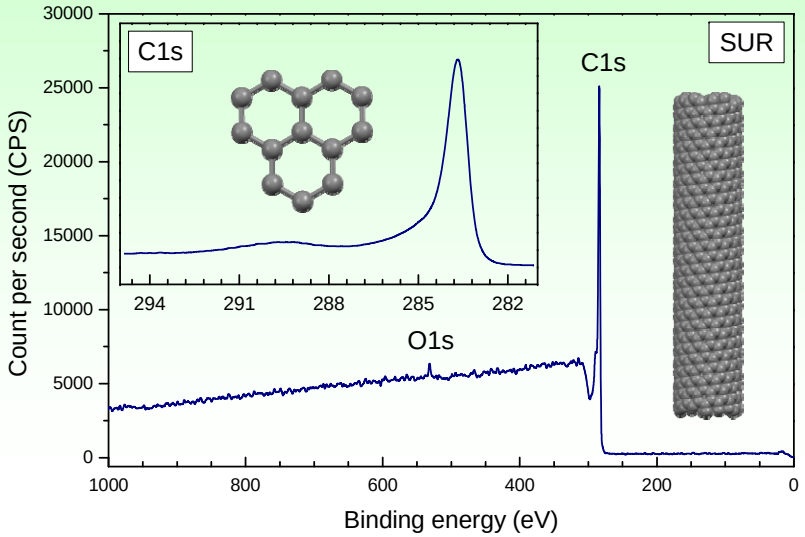


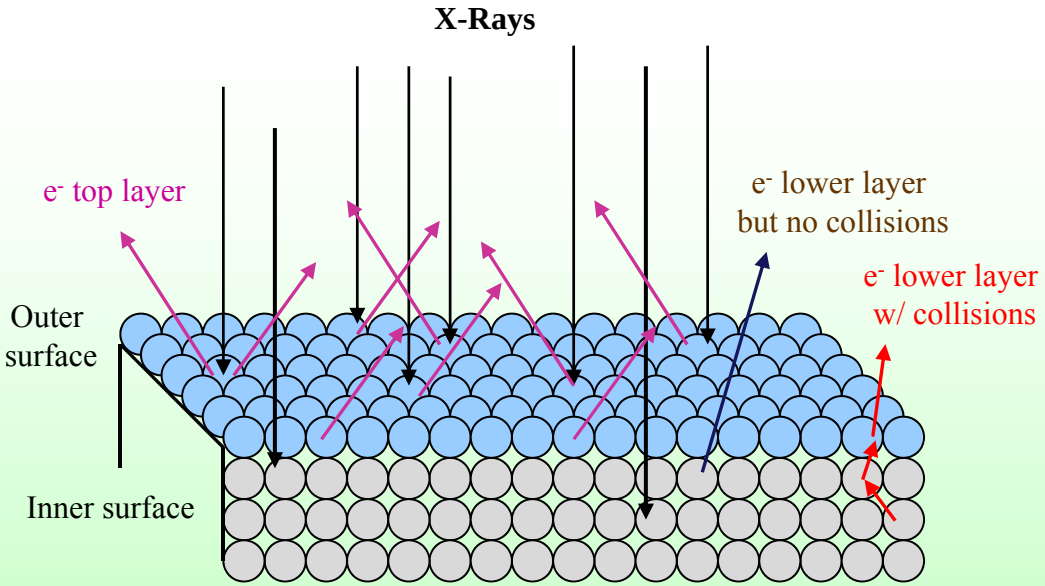
日東分析センタHPより，http://www.natc.co.jp/index.html

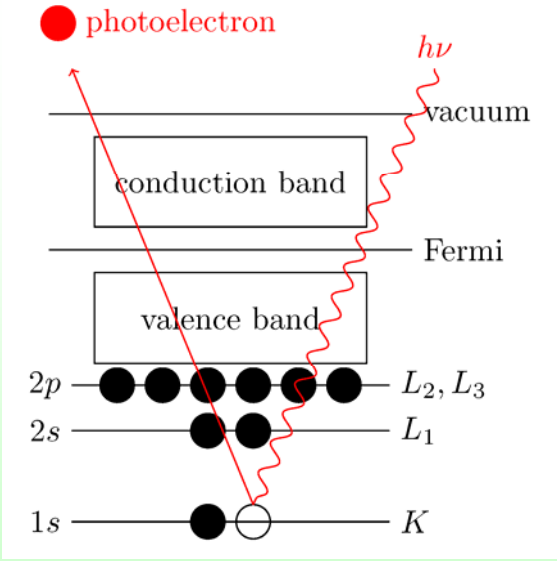
X-ray photoelectron spectroscopy (XPS)

Characteristic

- ❖ X-ray penetrate to core e⁻ of atoms
- ❖ Some e⁻ releasing characteristic K.E. of element
- ❖ Collided electrons from inner layers : lower K.E./noise
- ❖ Very surface sensitive process (~10 nm)





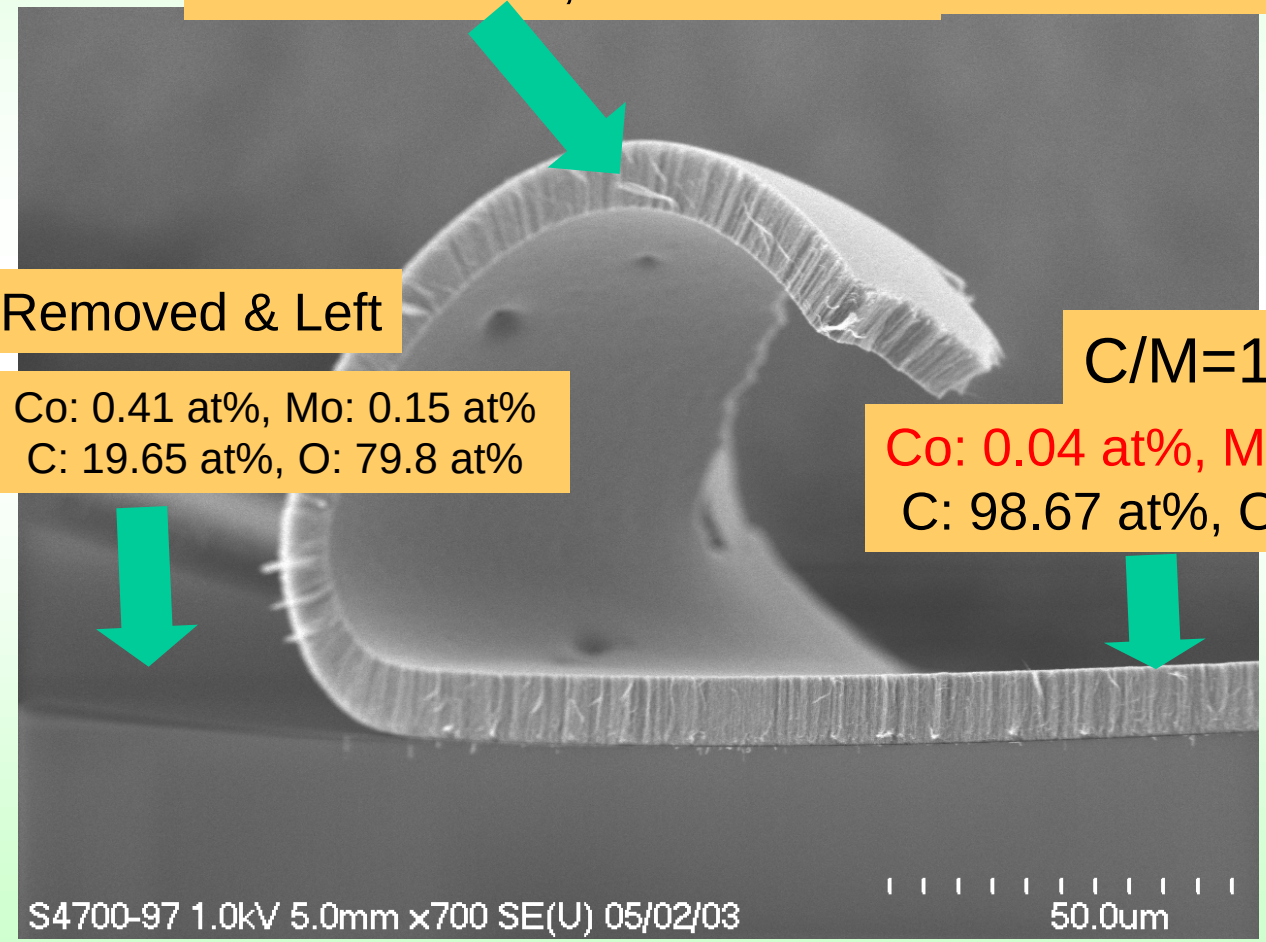


Demonstration of Root Growth and Yield by XPS

Root Side

Co: 0.05 at%, Mo: 0.03 at%
C: 91.23 at%, O: 8.69 at%

C/M=114,000



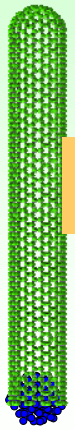
Removed & Left

Co: 0.41 at%, Mo: 0.15 at%
C: 19.65 at%, O: 79.8 at%

C/M=197,300

Co: 0.04 at%, Mo: 0.01 at%
C: 98.67 at%, O: 1.29 at%

Tip Side



(10,10) x 5 μm
=813,005 atoms

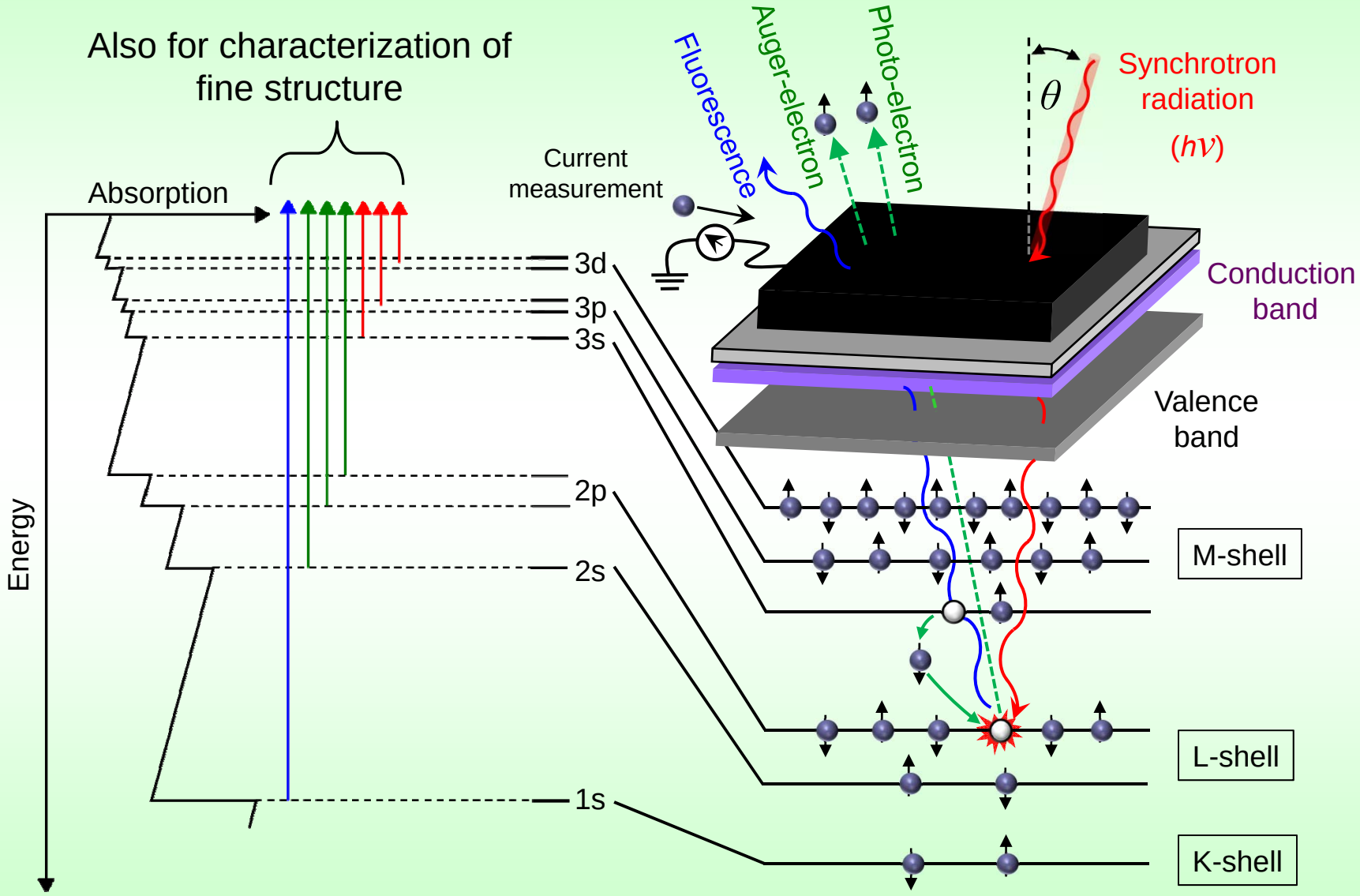
C/M = 271000

Metal of 1.3 nm
= 300 atoms

Hatas's SuperGrowth
0.013Fe
Supergrowth:50,000 wt%

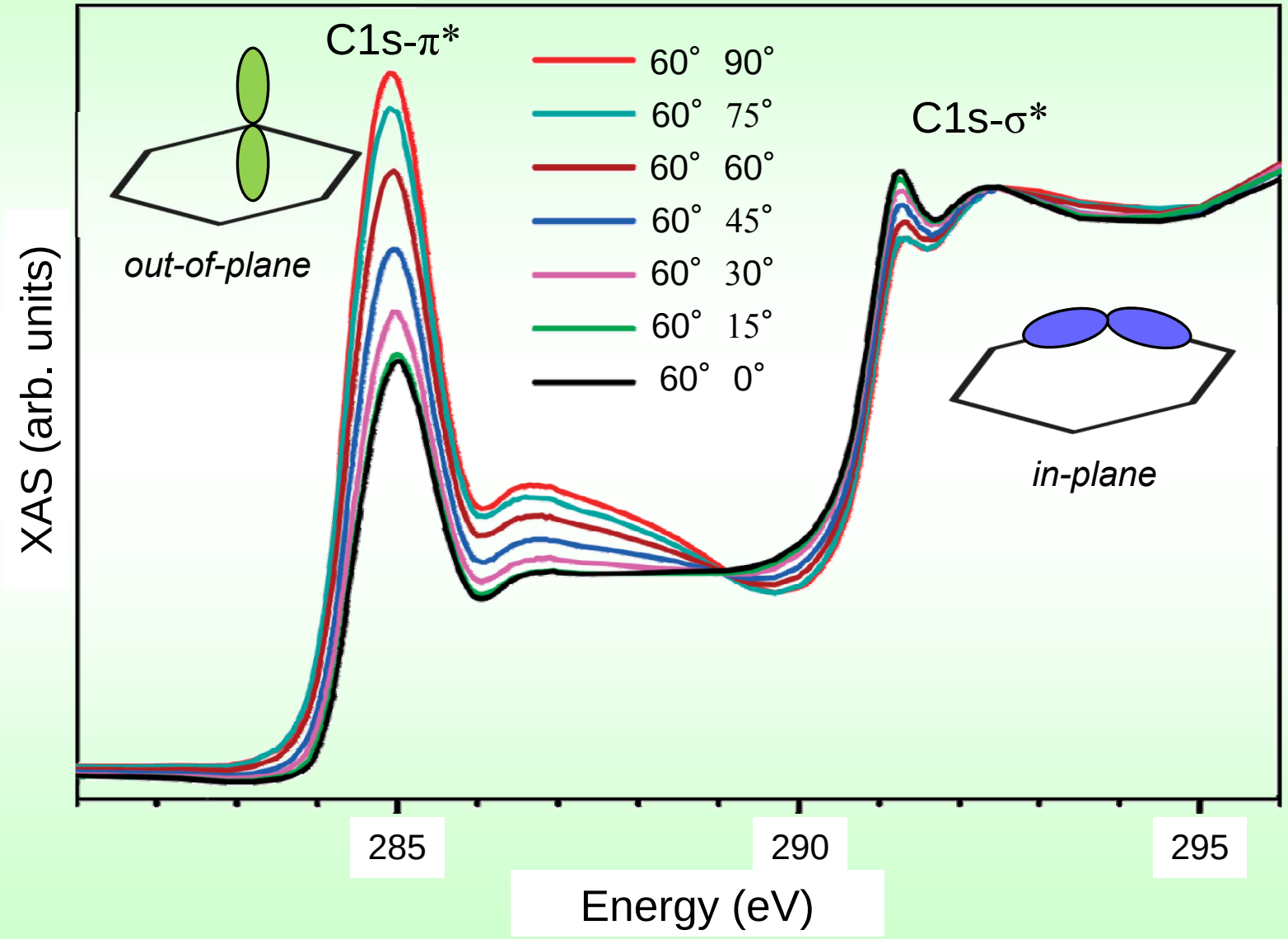
Acknowledgement to Shimazu for the use of KRATOS (AXIS-NOVA)

X-ray absorption spectroscopy (XAS)



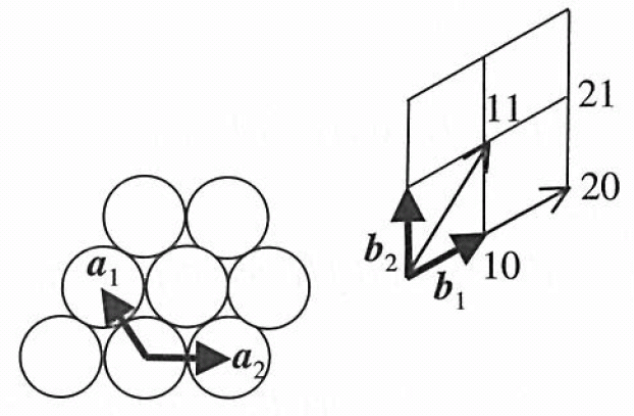
http://en.wikipedia.org/wiki/X-ray_absorption_spectroscopy

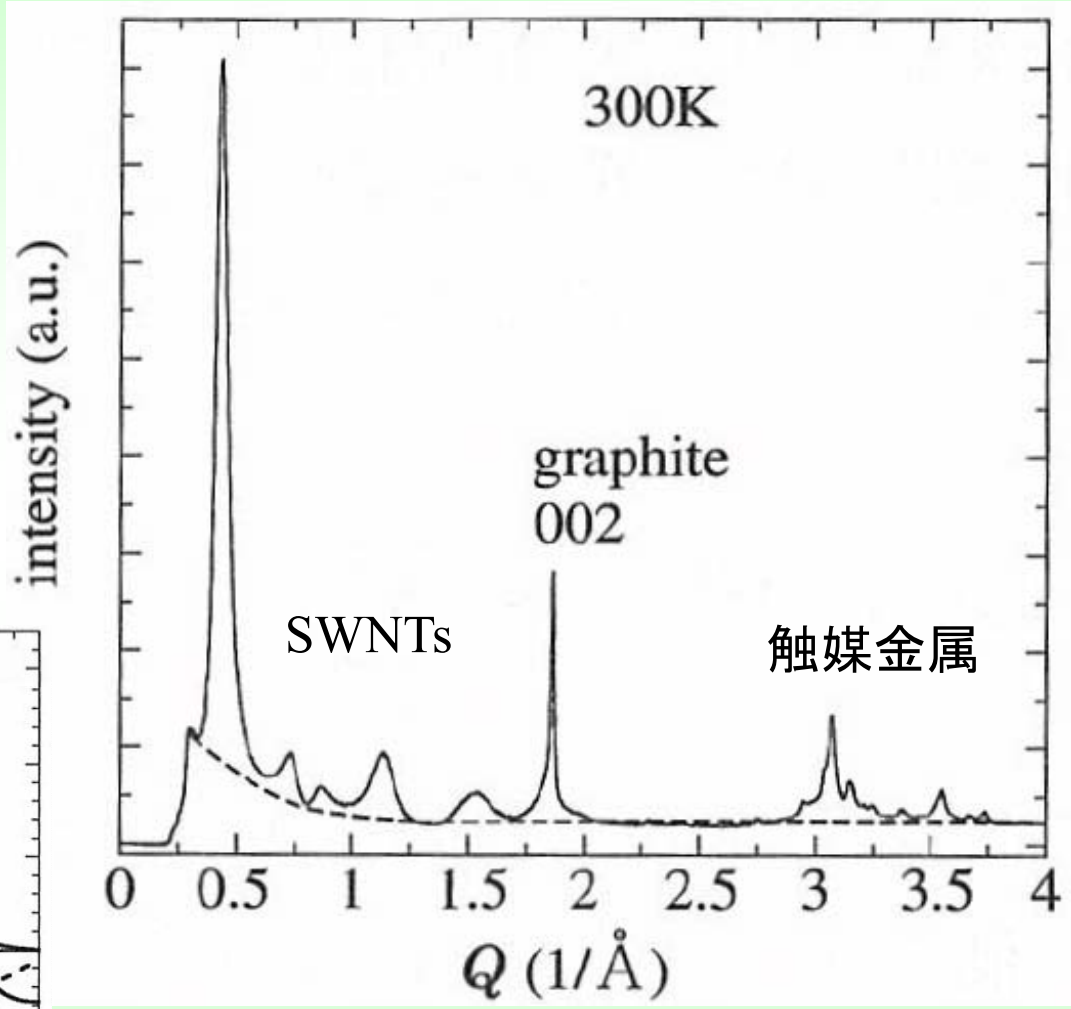
Near-edge X-ray absorption fine structure (NEXAFS) of SWNTs

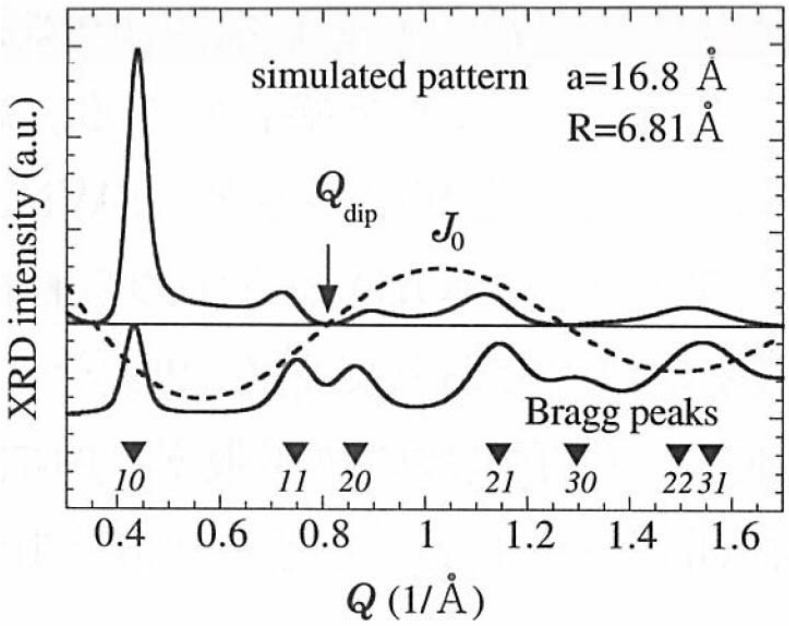


C. Kramberger et al., *Phys. Status Solidi. B* **244** (2007) 3978.

X-Ray Diffraction







真庭　豊，カーボンナノチューブの基礎と応用，培風館