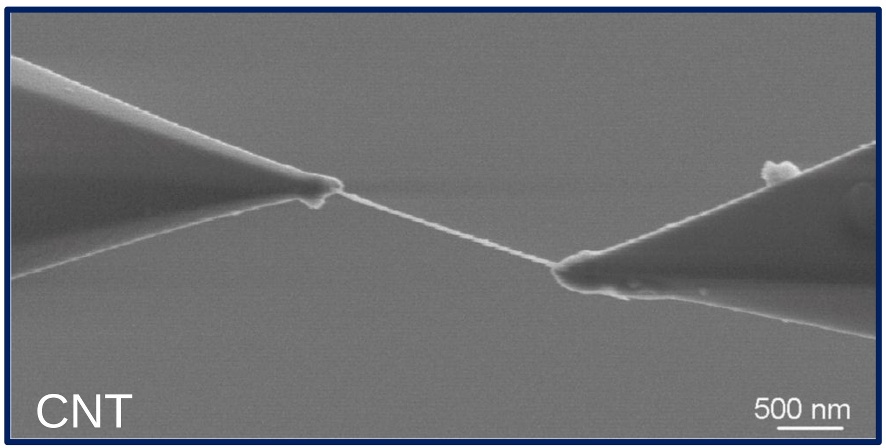
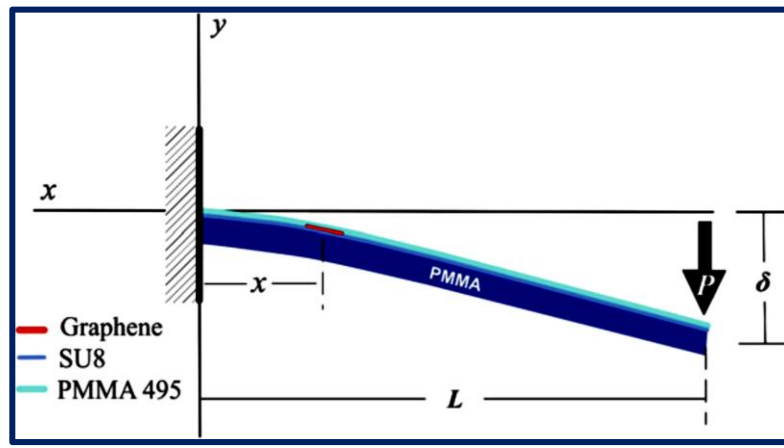
Η δονητική φασματοσκοπία και οι μηχανικές μετρήσεις στη νανοτεχνολογία

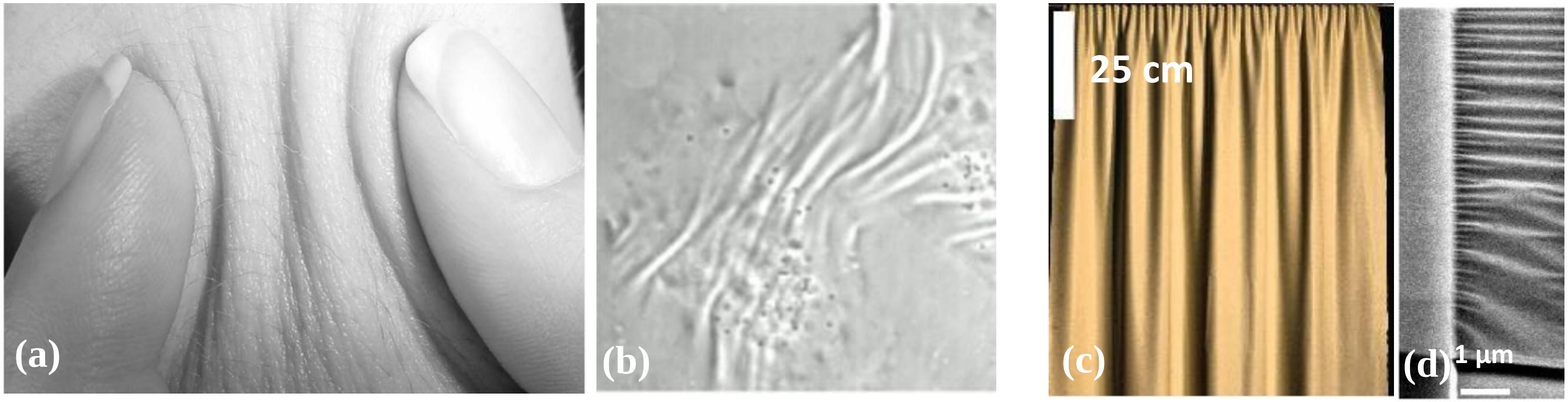
Δρ Ι. Παρθένιος

Κύριος Ε. Λ. Ε., ΙΤΕ/ΙΕΧΜΗ



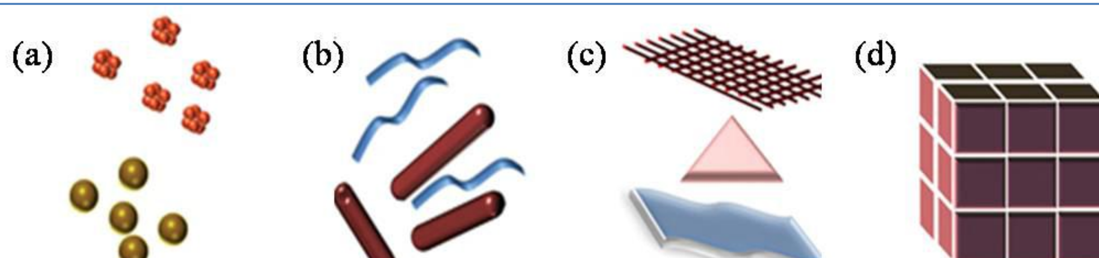


From macro to nano



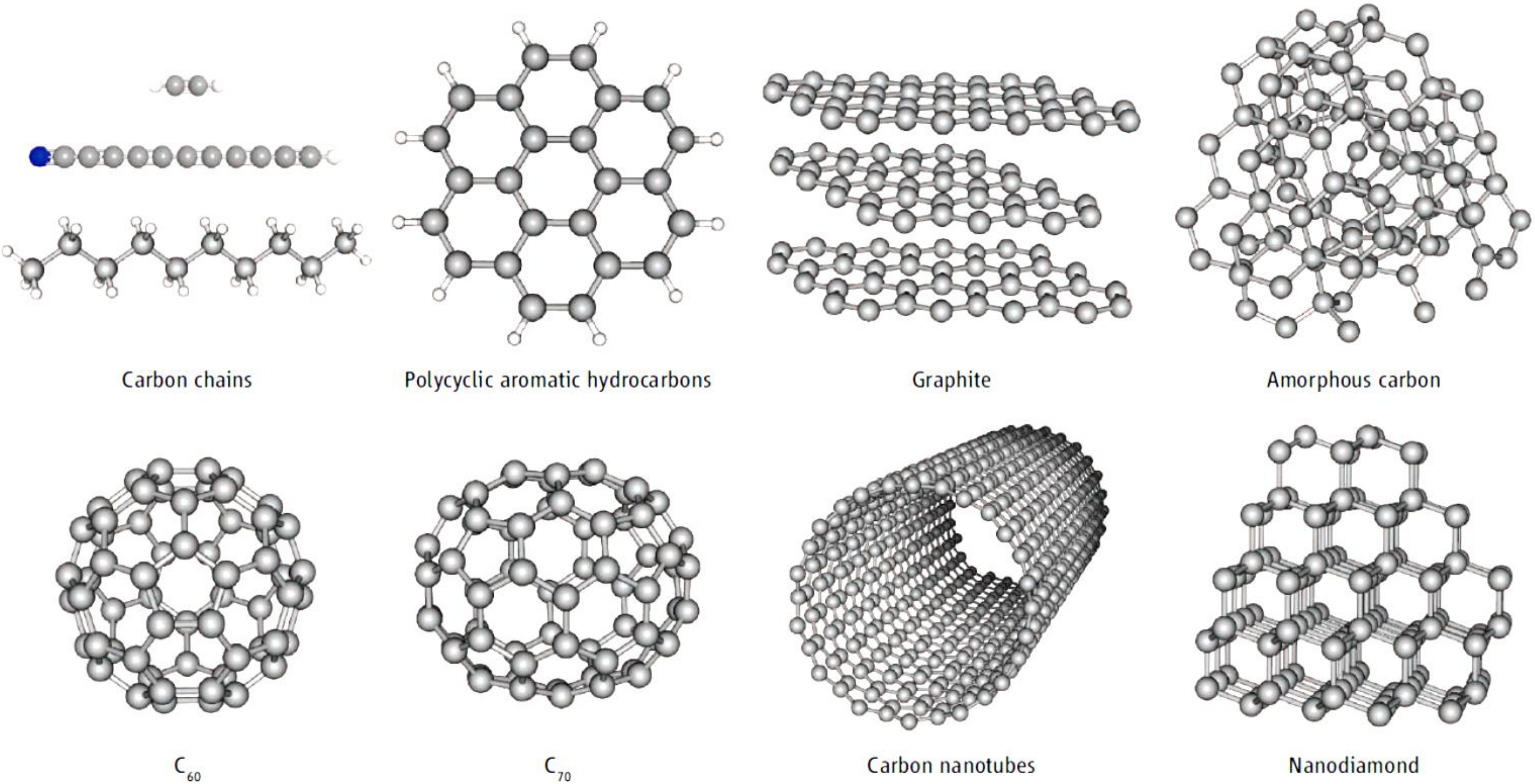
Human Skin | **Human Cell on Si** | **House Curtains** | **Bilayer Graphene** *(t ~ 0.7 nm)*

Vandeparre H., *et al.* PRL, 106, 224301 (2011)



0D **1D** **2D** **3D**

Various forms of carbon-based nanomaterials



P. Ehrenfreund and B. H. Foing, *Science* 329, 1159 (2010)

Mechanical characterization of nanomaterials

MWCNT

Force = *kd* ~ *400 – 1340 nN*
Strain = δL/L

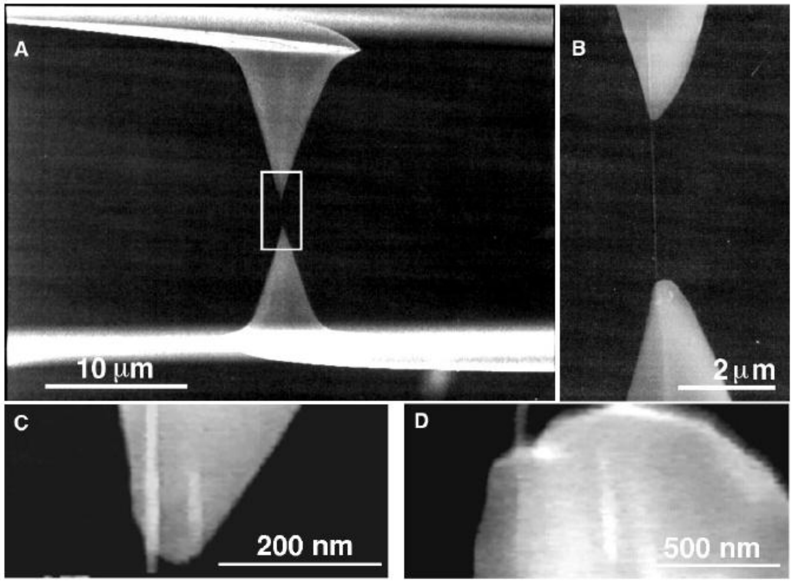
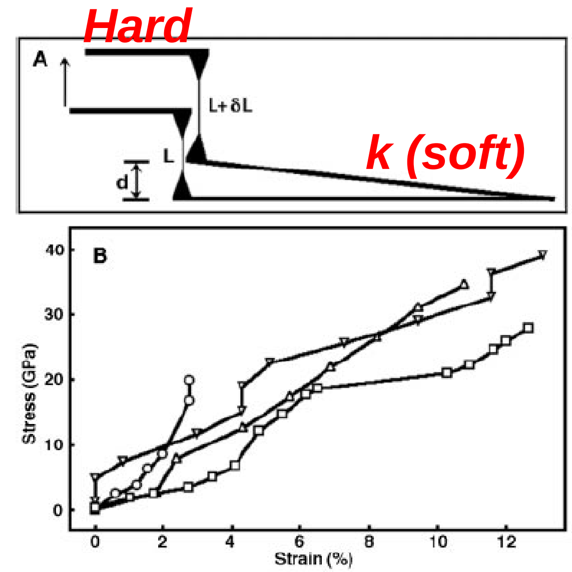


Fig. 1. An individual MWCNT mounted between two opposing AFM tips. (**A**) An SEM image of two AFM tips holding a MWCNT, which is attached at both ends on the AFM silicon tip surface by electron beam deposition of carbonaceous material. The lower AFM tip in the image is on a soft cantilever, the deflection of which is imaged to determine the applied force on the MWCNT. The top AFM tip is on a rigid cantilever that is driven upward to apply tensile load to the MWCNT. (**B**) High-magnification SEM image of the indicated region in (A), showing the MWCNT between the AFM tips. (**C**) Higher magnification SEM image showing the attachment of the MWCNT on the top AFM tip. There is an apparent thickening of the MWCNT section on the surface. (**D**) Close-up SEM image showing the attachment of the MWCNT on the lower AFM tip. The MWCNT section is covered by a square-shaped carbonaceous deposit.

Fig. 2 (**A**) Schematic showing the principle of the tensile-loading experiment. When the top cantilever is driven upward, the lower cantilever is bent upward by a distance *d*, while the nanotube is stretched from its initial length of *L* to *L* + δ*L* because of the force exerted on it by the AFM tips. The force is calculated as *kd*, where *k* is the force constant of the lower cantilever. The strain of the nanotube is δ*L*/*L*. (**B**) Plot of stress versus strain curves for individual MWCNTs. The *E* values in Table 1 are as follows: 954 GPa from a linear fit to the upswing part of the curve for nanotube 2 (O); linear fits of the first (470 GPa) and the second (300 GPa) upswings for nanotube 15 (□), and 335 and 274 GPa from linear fits of the whole curve for nanotubes 18 (Δ) and 19 (∇).

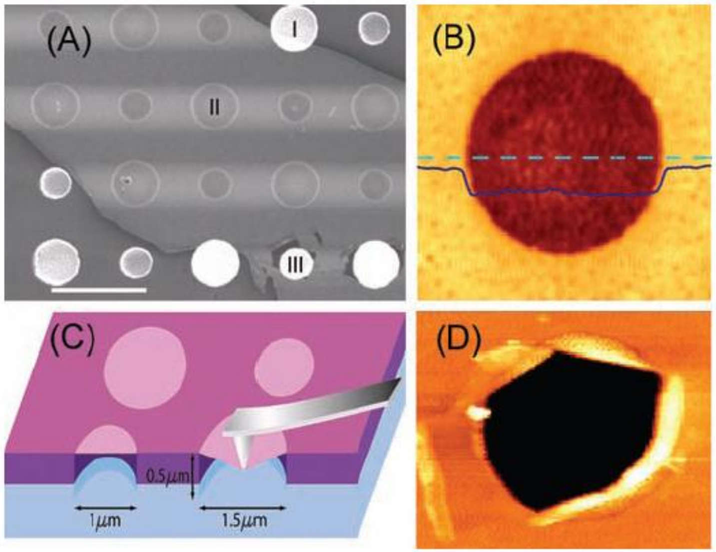


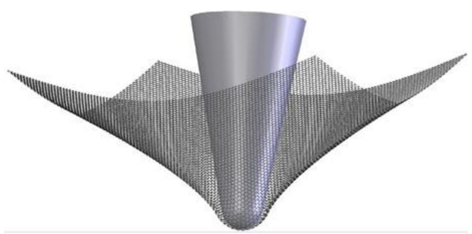
Fracture strength: 11-63 GPa
Strain at break: ~12%
Young's Modulus: 274 to 954 GPa

Yu MF, Lourie O, Dyer MJ, Moloni K, Kelly TF, and Ruoff RS, **Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load,** *Science*, 287, 637-640 (2000).

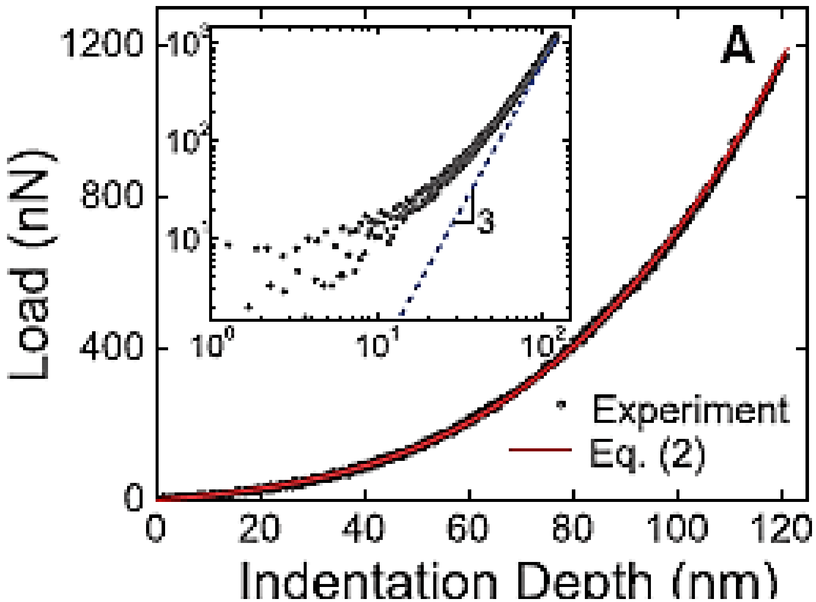
Mechanical characterization of nanomaterials

Graphene





AFM nanoindentation of graphene membrane



$$F = \sigma_0^{2D}(\pi a)\left(\frac{\delta}{a}\right) + E^{2D}(q^3 a)\left(\frac{\delta}{a}\right)^3 \qquad (2)$$

Max deflection δ ~ 100 nm

The elastic properties and intrinsic breaking strength of ‘defect-free’ monolayer

Breaking strength ~ 42 N/m

Young’s modulus ~1.0 Tpa

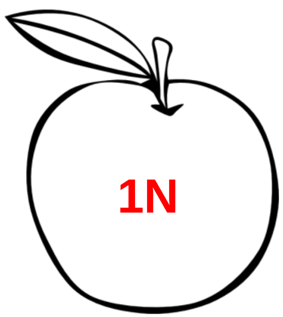
Tensile Strength ~ 130 GPa

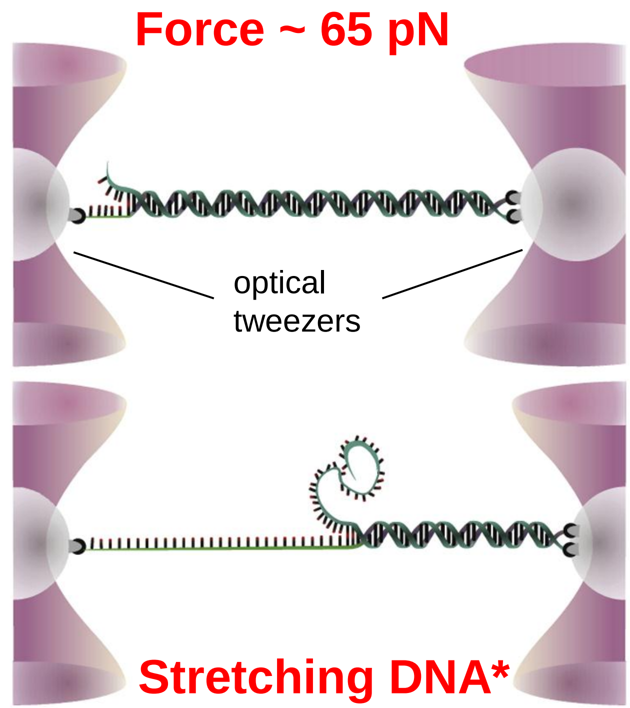
Lee, et al., *Science*, 321, (2008), 385-388

Force to break a covalent bond in graphene

$$\boxed{F_{bond} = \text{Breaking strength} \times \text{deformation} = \left(42\ Nm^{-1}\right)\left(0.142\ nm\right) \approx 6\ nN}$$

- It is assumed that the deformation for bond breaking of the C-C bond in graphene is ~ 0.142 nm

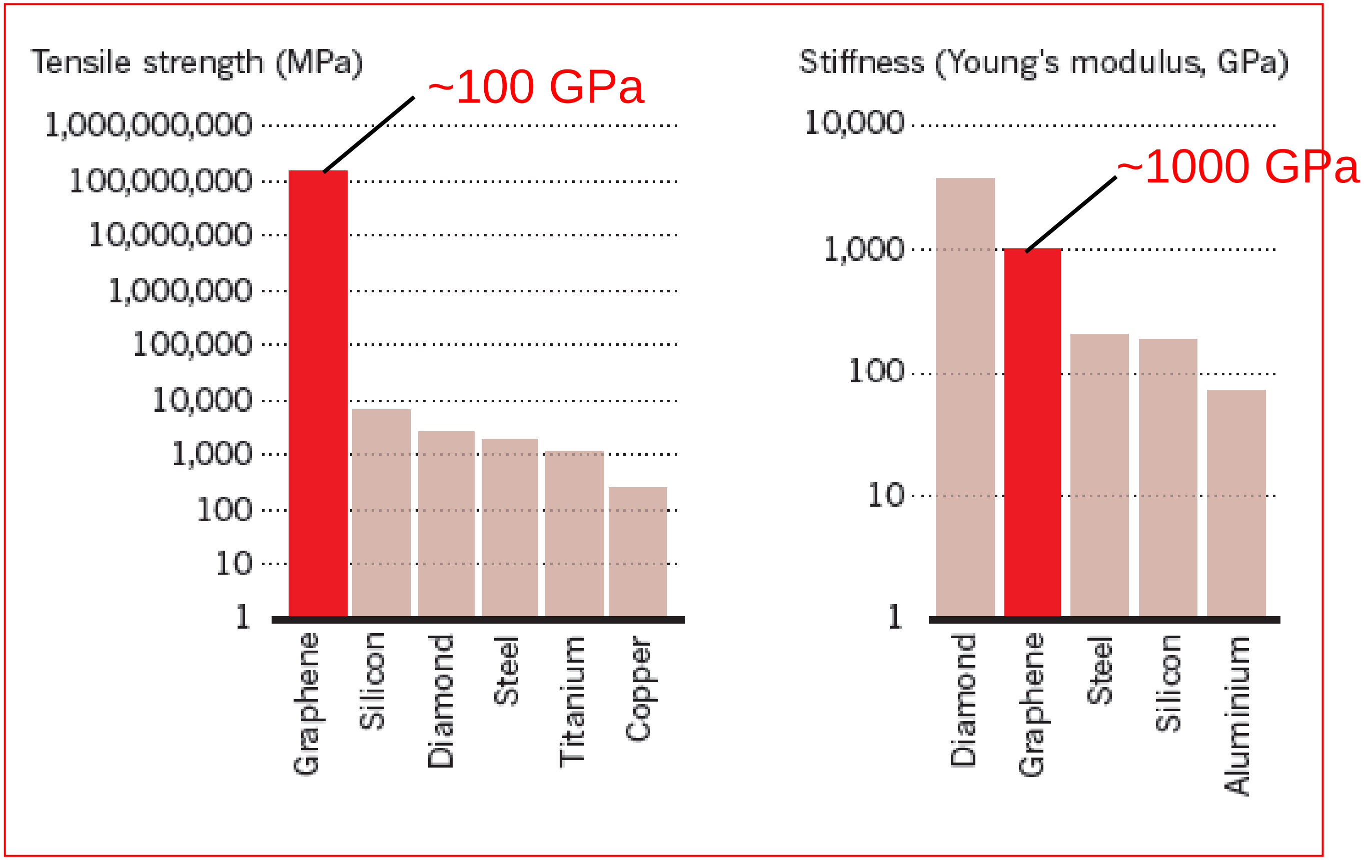




- Need: Precise force measurement

*Gross, P. et al. **Quantifying how DNA stretches, melts and changes twist under tension**. *Nature Physics* 7, 731–736 (2011).

Tensile strength and stiffnes of materials – A comparison



Raman spectroscopy in Nanomechanics

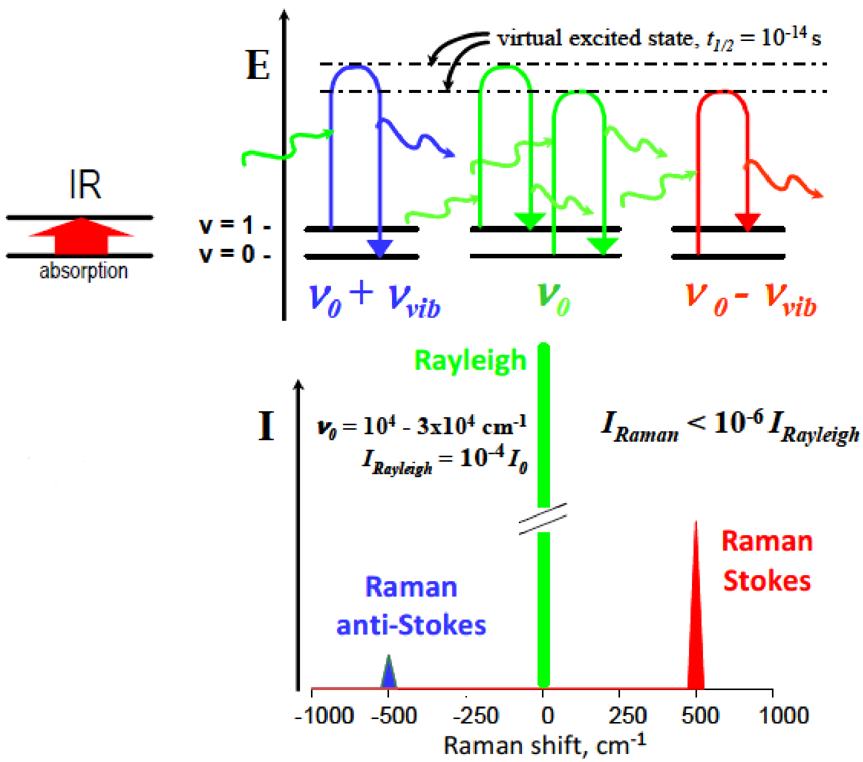
Raman scattering

$$P_{Scattered} = \sigma_R I_o$$

$$\sigma_R = \frac{8\pi\omega_s^4}{9\hbar c^4}\left|\sum_j\left[\frac{M_{initial,j}M_{j,final}}{\omega_{initial,j}-\omega_p-i\Gamma_j}+\frac{M_{j,initial}M_{j,final}}{\omega_{j,final}-\omega_p-i\Gamma_j}\right]\right|^2$$

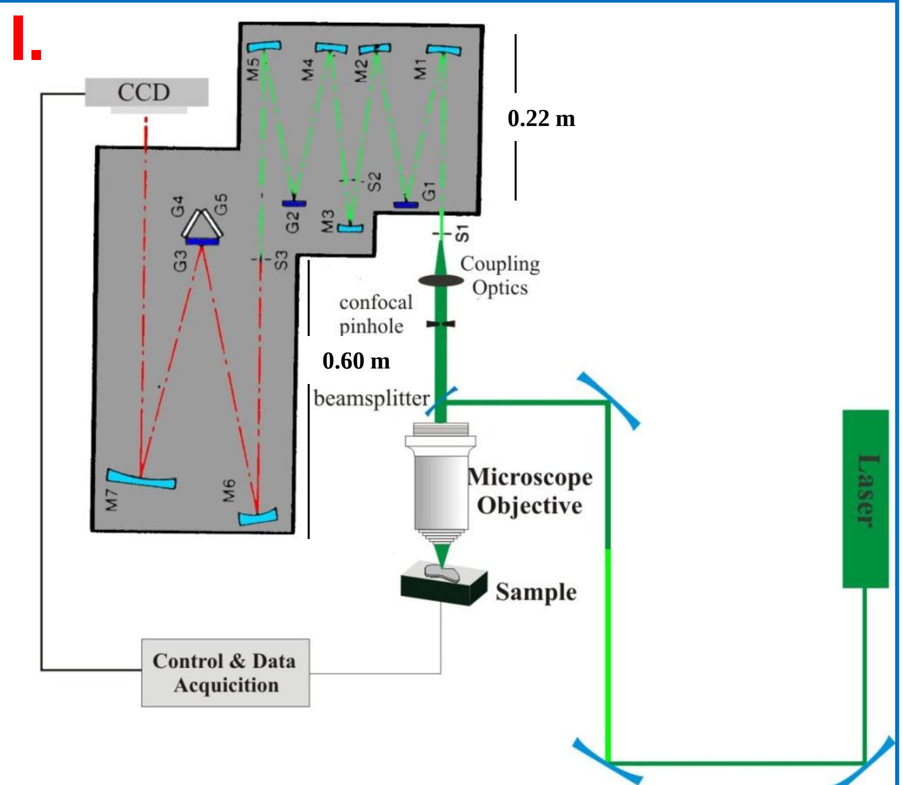
$$P_{Scattered} \propto \frac{I_o}{\lambda^4}$$

The Raman effect comprises a very small fraction, about 1 in 10^7, of the incident photons

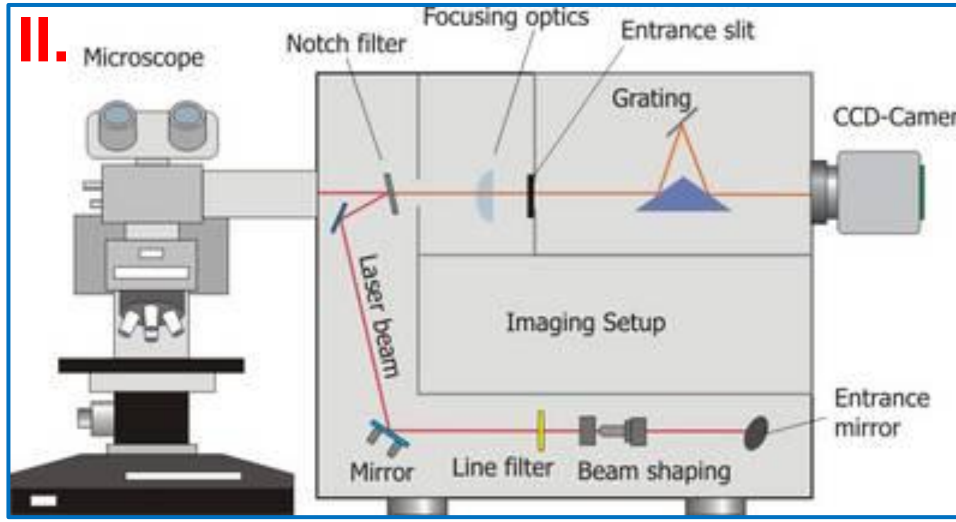


- Energy conservation: $\pm\hbar\omega_s = \varepsilon_i - \varepsilon_f$
- Momentum conservation: $\pm\mathbf{k} = \mathbf{k}_i - \mathbf{k}_f$

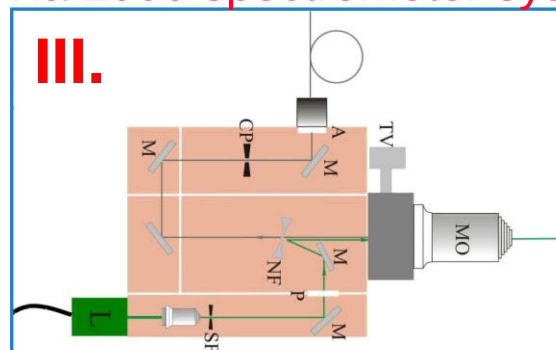
Experimental set-ups



Jobin Yvon microscope/Spex Triplemate 0.6m



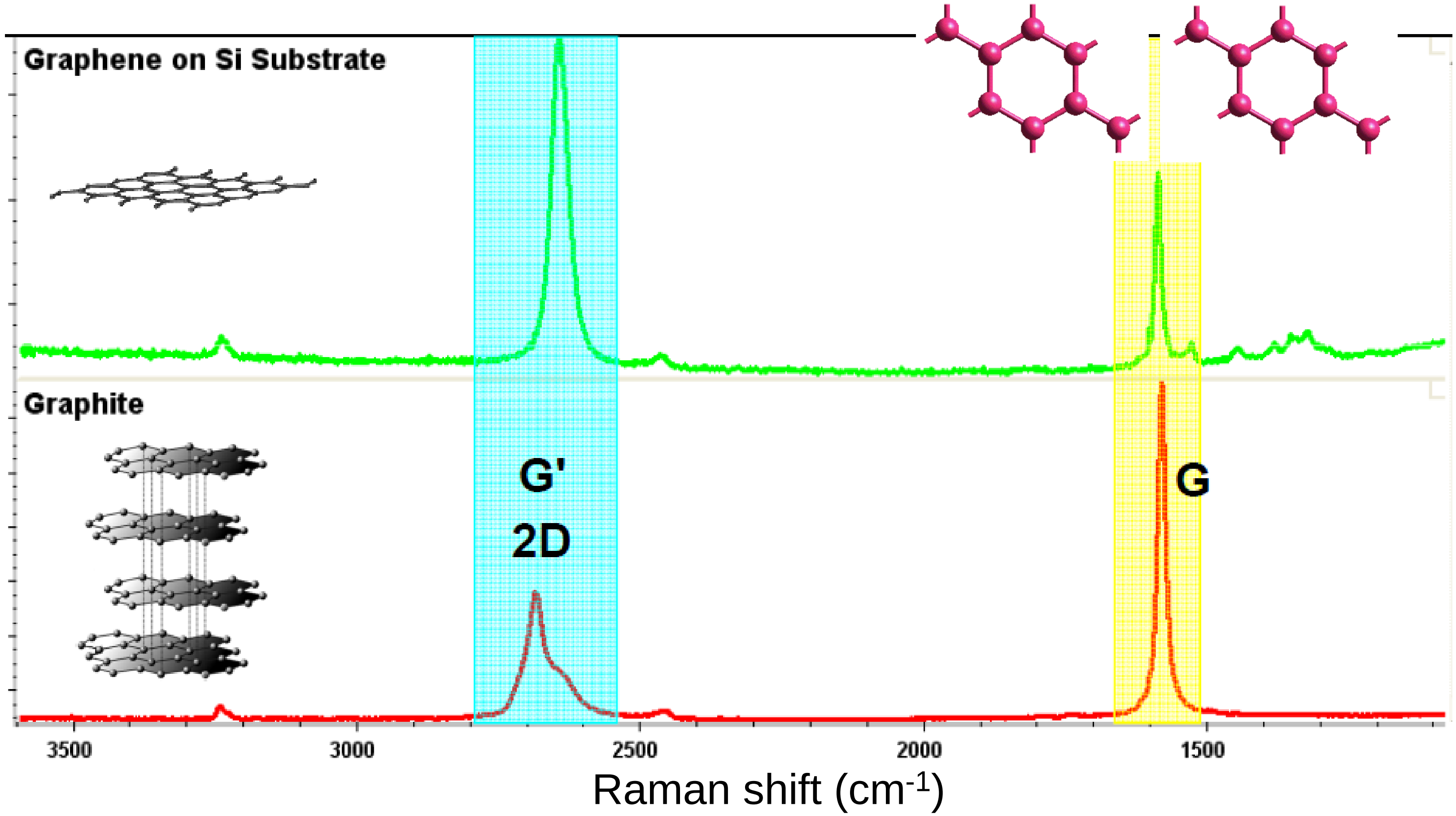
Renishaw inVia 2000 spectrometer system



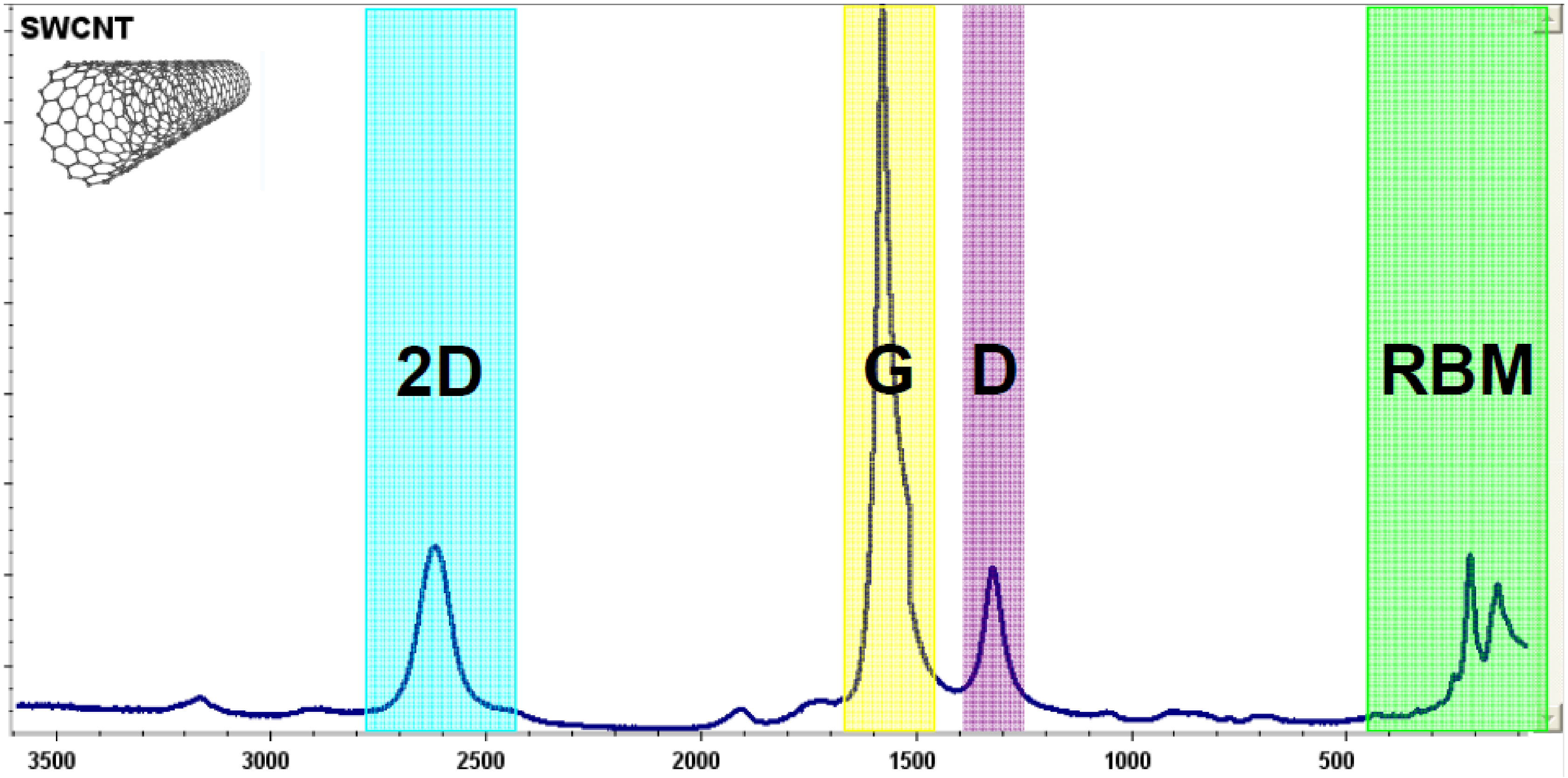
Remote Raman System

A: Analyzer
CP: Adjustable Confocal Pinhole
DF: Delivery Fiberoptic (To portable spectrometer)
L: DPSS Laser @ 523 nm (Internal laser source)
M: Mirror
MO: Microscope Objective
NF : Notch Filter
P: Polarizer
SF: Spatial filter
TV: CCTV

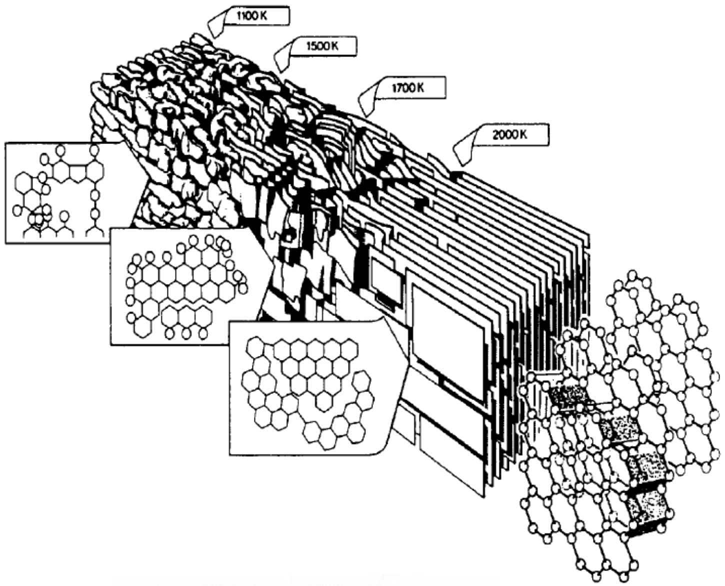
Raman spectra of graphitic materials - 2D

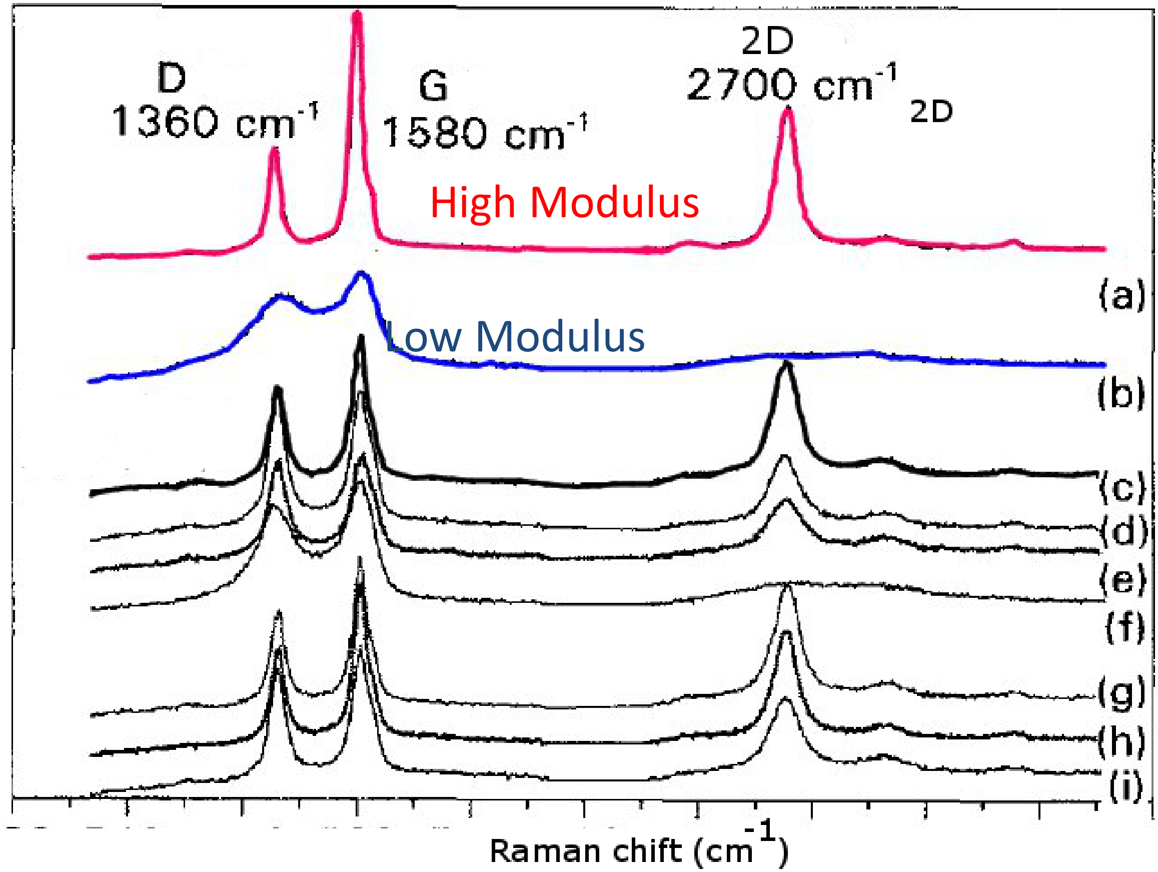


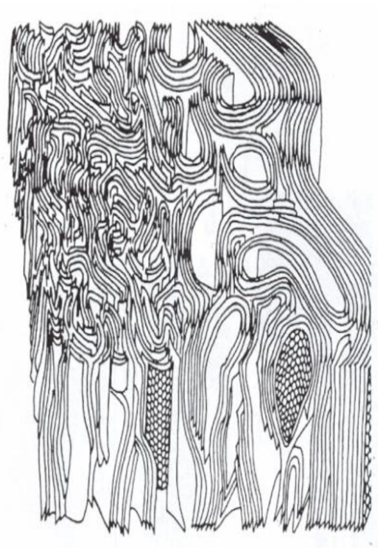
Raman Spectrum of SWCNT – 1D



CF Structure Development and the corresponding Raman spectra of carbon fibres -3D



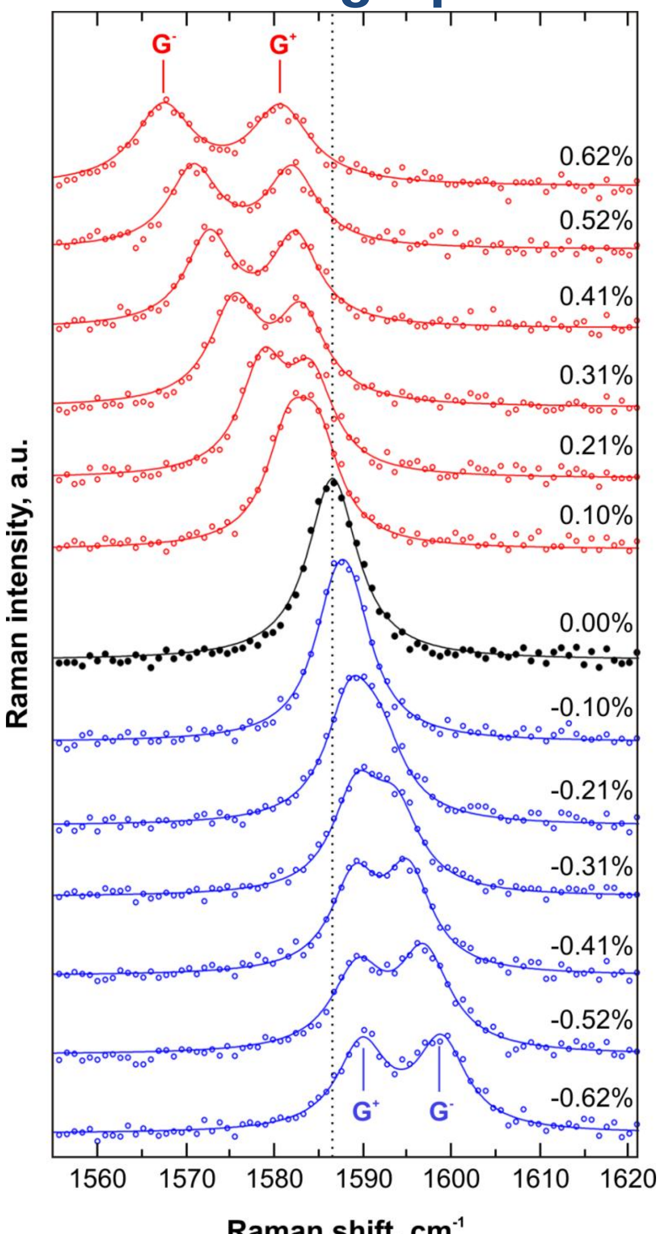


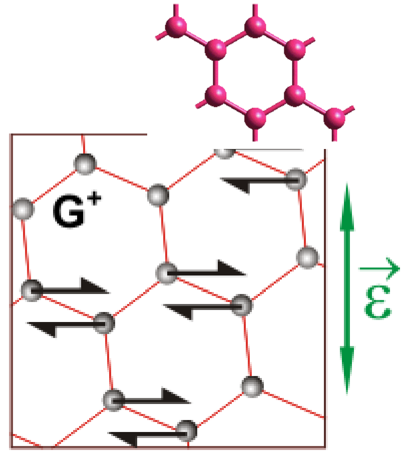


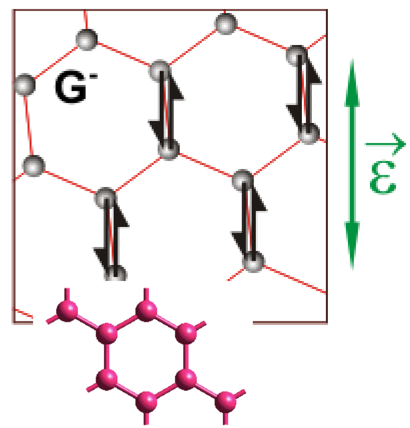
Carbon fibres (microscale)

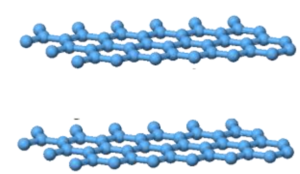
(Source: A. R. Bunsell, Fibre Reinforcements for Composite Materials, Amsterdam, The Netherlands: Elsevier Science Publishers B.V., 1988, p. 120.)

G-band of graphene under Strain in Tension & Compression



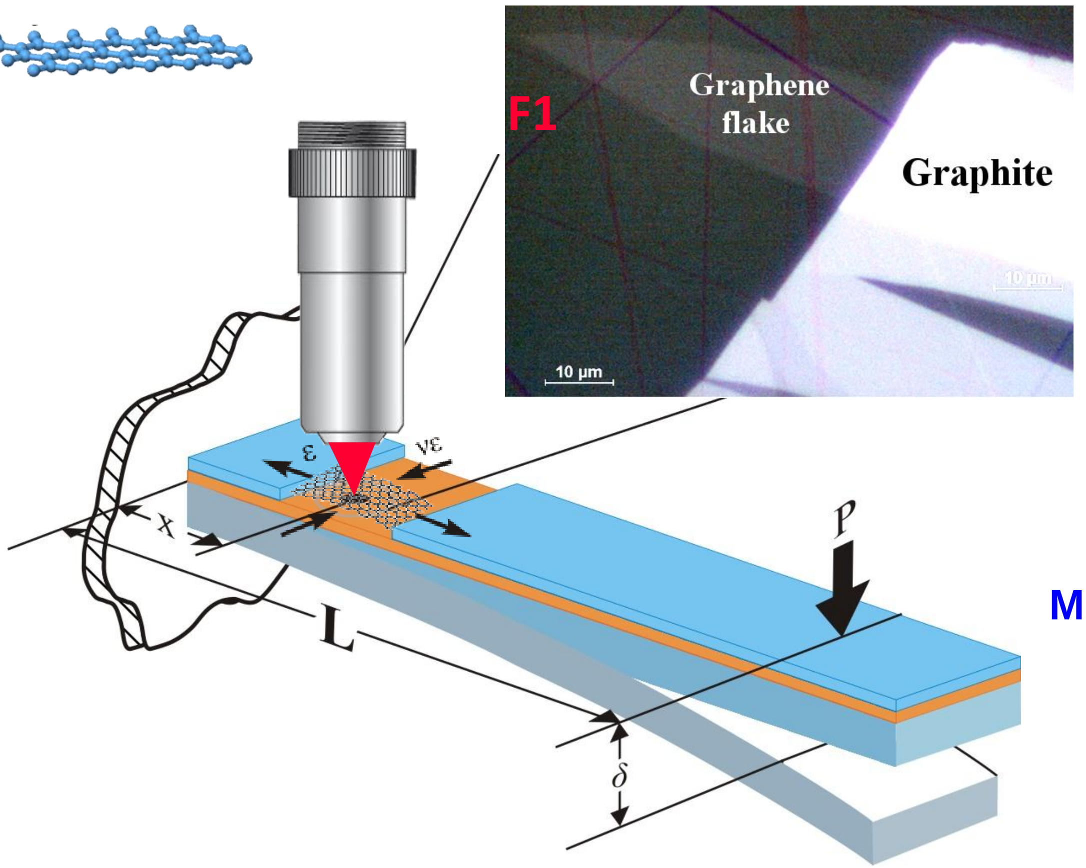




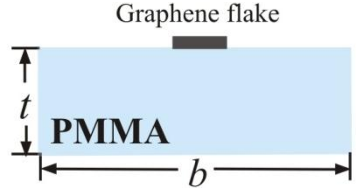


Axial Experiments in Graphene
(tension & compression combined with Raman measurements)

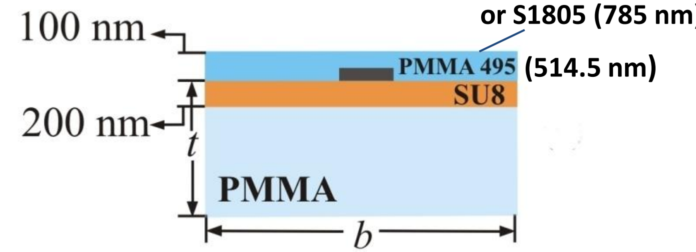
Experimental Set-up for Application of Uniaxial Strain



Simply-supported flake



Embedded flake



Mechanical strain at the top of the beam

$$\varepsilon(x) = \frac{3t\delta}{2L^2}\left(1 - \frac{x}{L}\right)$$

δ: deflection of the beam neutral axis
L: span of the beam
t : beam thickness

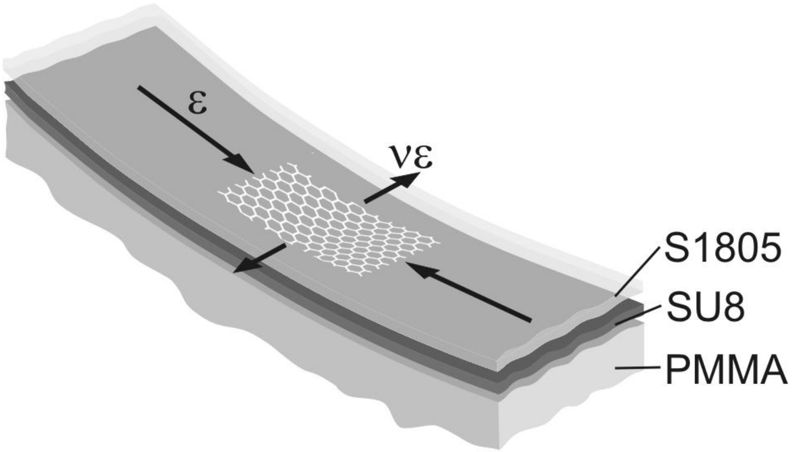
Materials & Geometry

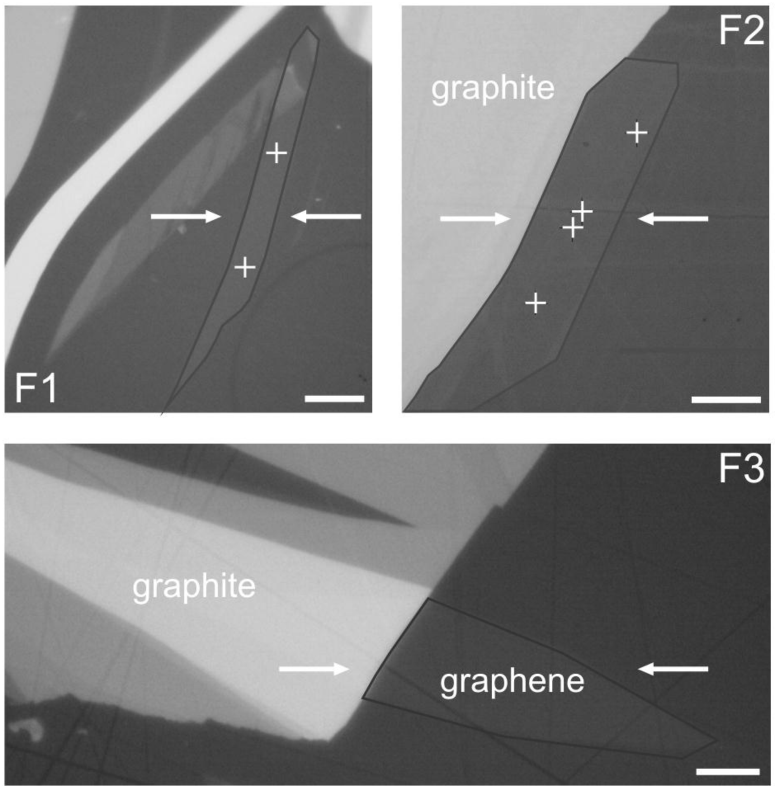
- SU8 photo resist epoxy-based polymer
- PMMA beam substrate (*2.9x12.0x70)* mm^3
- *x* = 10.4 mm and *L* = 70 mm

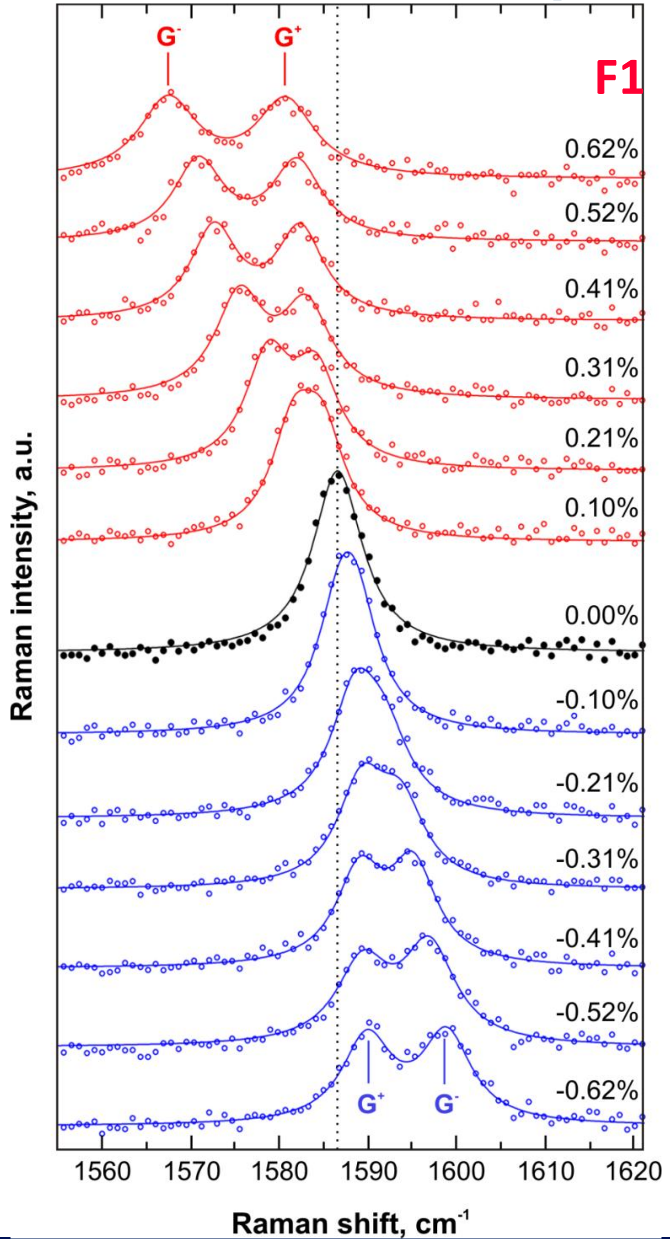
Operating limits:

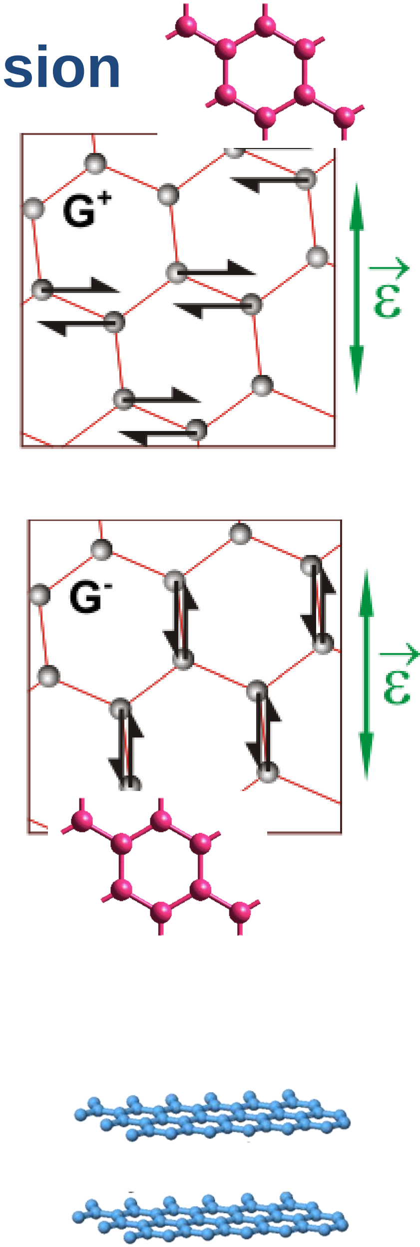
- L>> 10δ_{max}
- -1.5% < ε < 1.5%

G-band under Strain in Tension & Compression

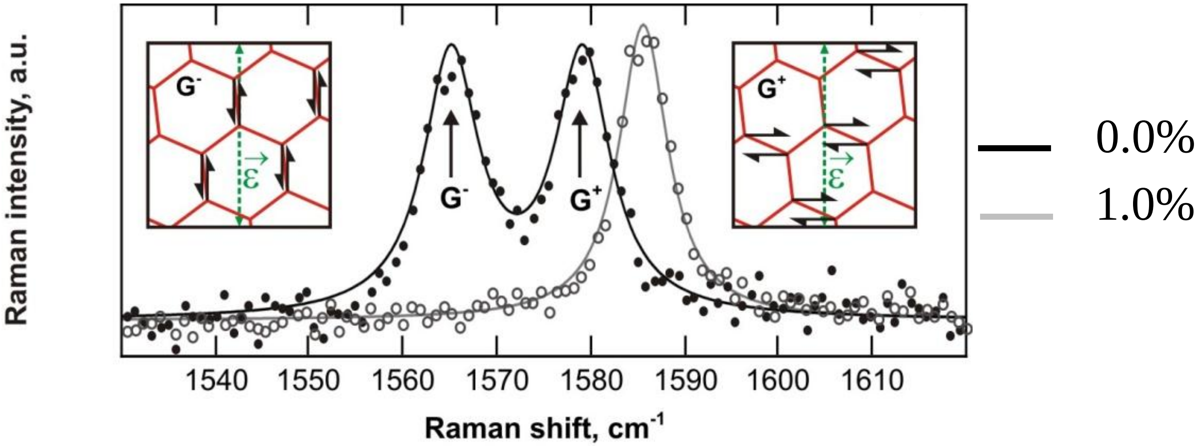


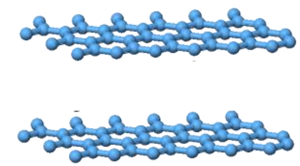


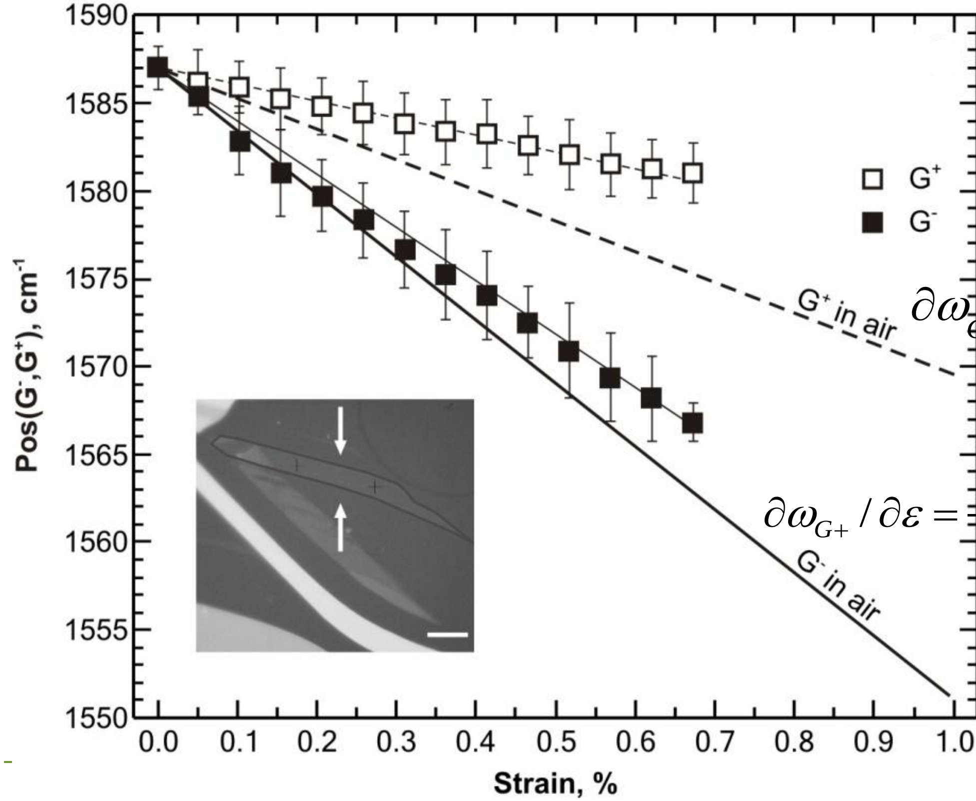




G-band vs. Strain (no residual strain)







$$\partial\omega_{G^-}/\partial\varepsilon = -36.0\,\mathrm{cm}^{-1}/\%$$

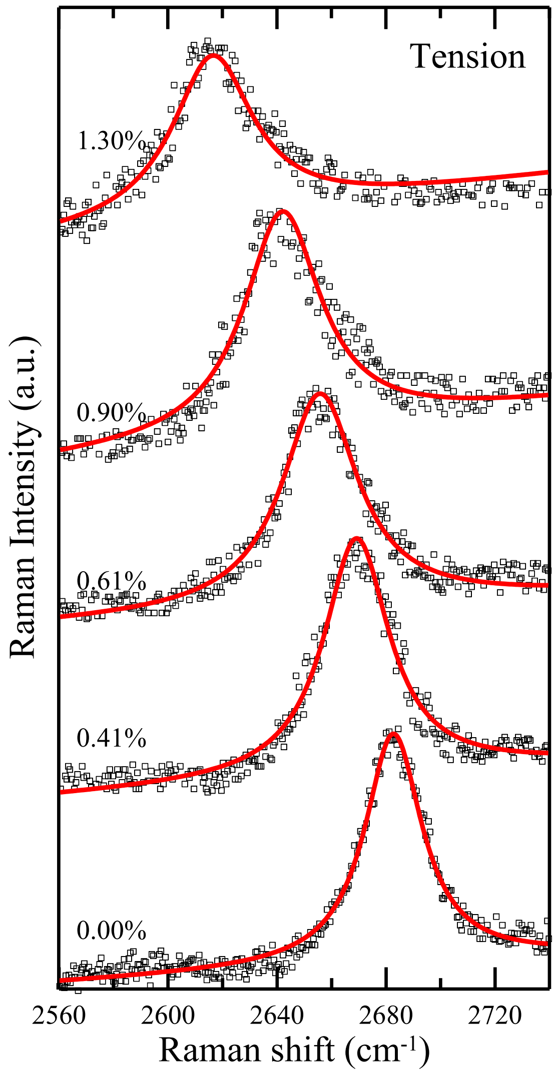
$$\partial\omega_{G+}/\partial\varepsilon = -17.5\,\mathrm{cm}^{-1}/\%$$

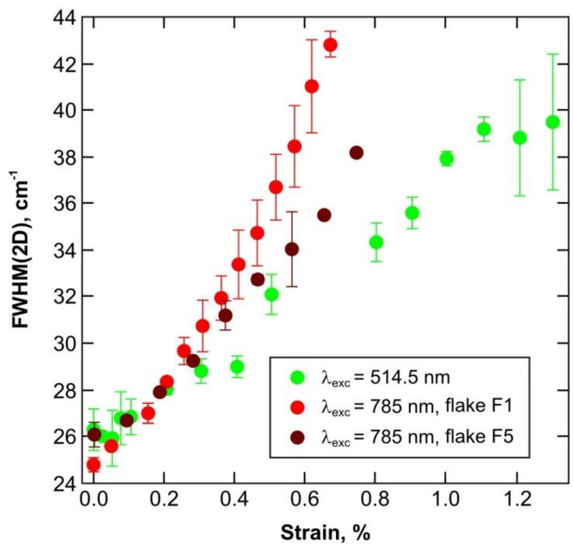
Mohiudin et al, PRB, **2009**

Frank et al, ACS-Nano, **2010**

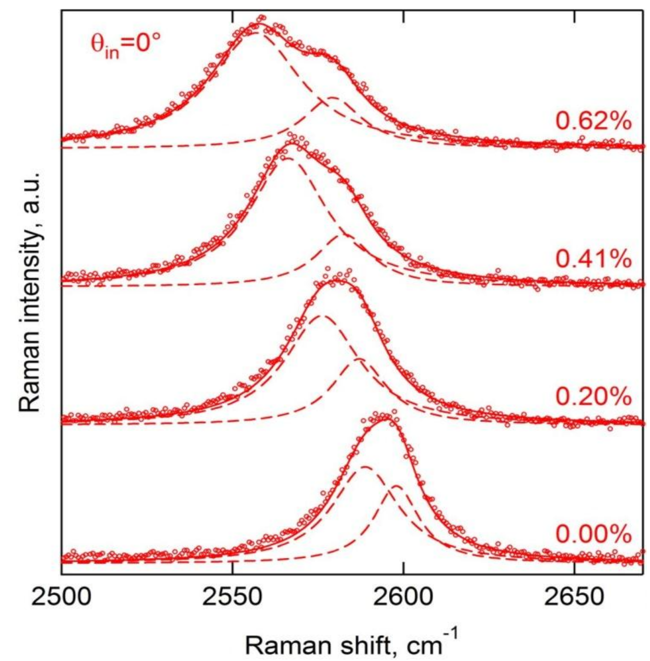
Raman 2D-peak splitting in single-layer graphene

λ=514.5 nm





λ=785 nm

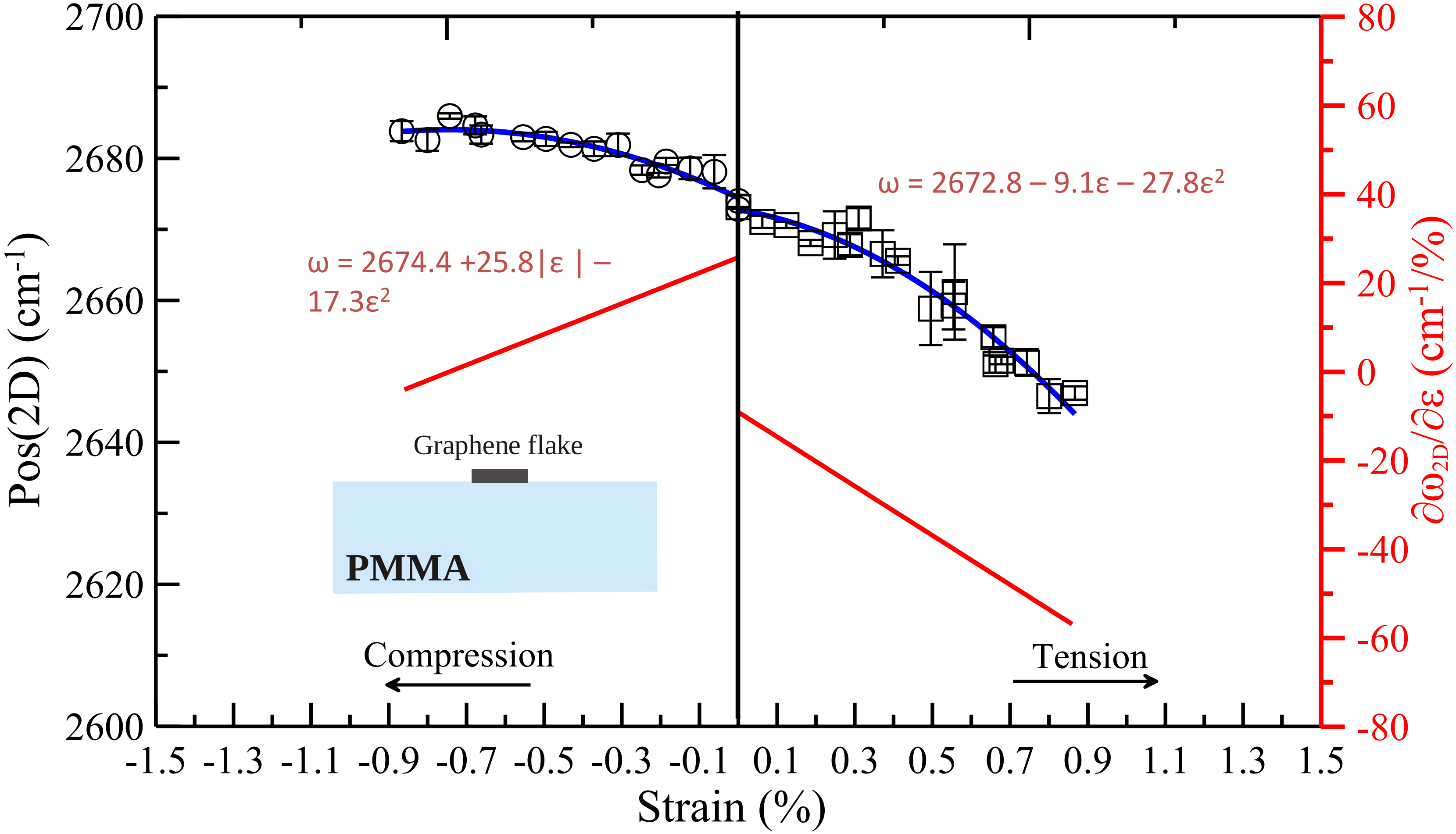


Measurements of the 2D band alone, for excitation energies lower than 2.41 eV (514.5 nm), may lead to errors with regards to the detailed determination state of stress/strain in the specimen.

Frank et al., *ACS-Nano*, 5, 2321 (2011)

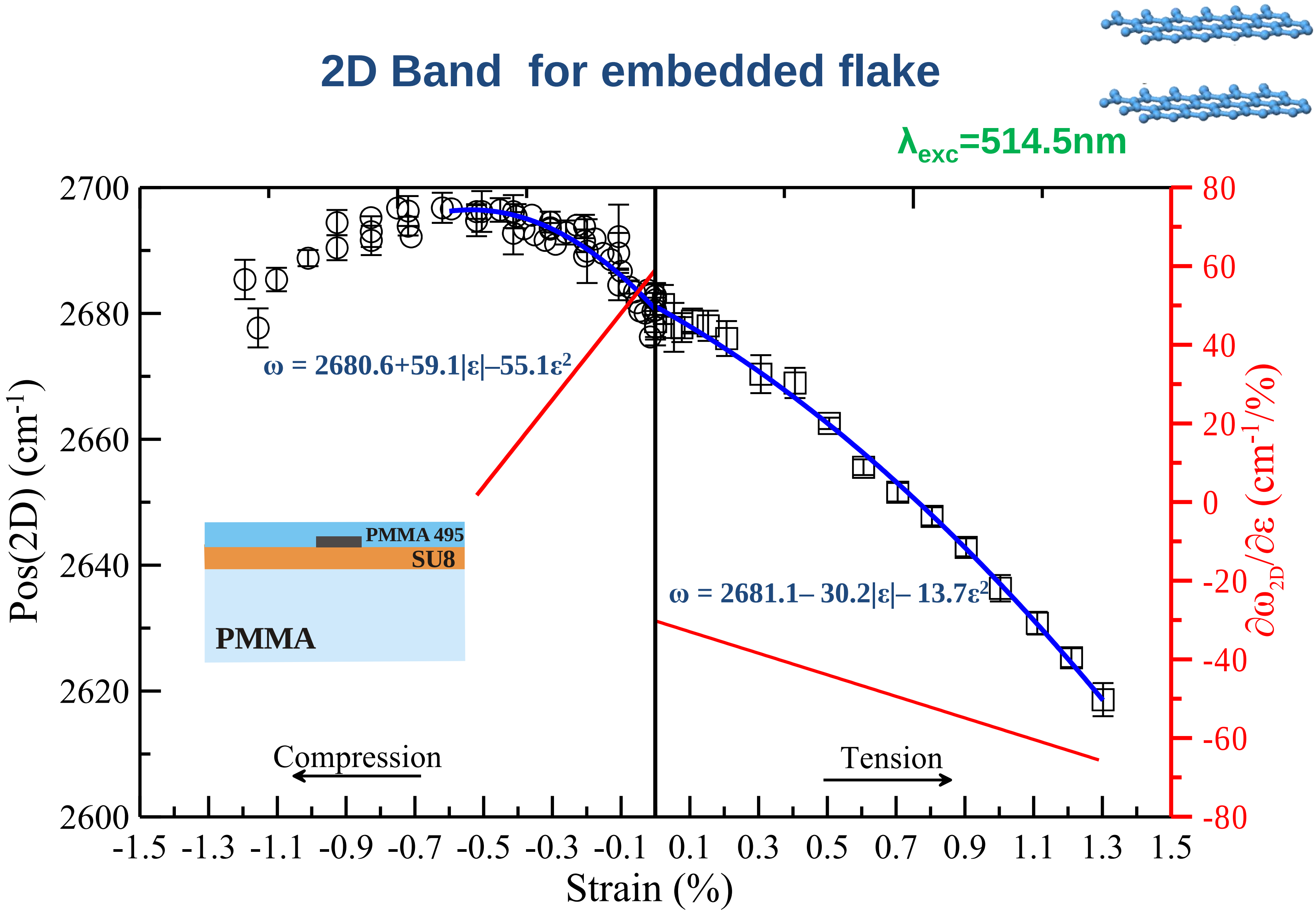
A simply-supported (“bare”) flake can be loaded!

λ_{exc}=514.5nm



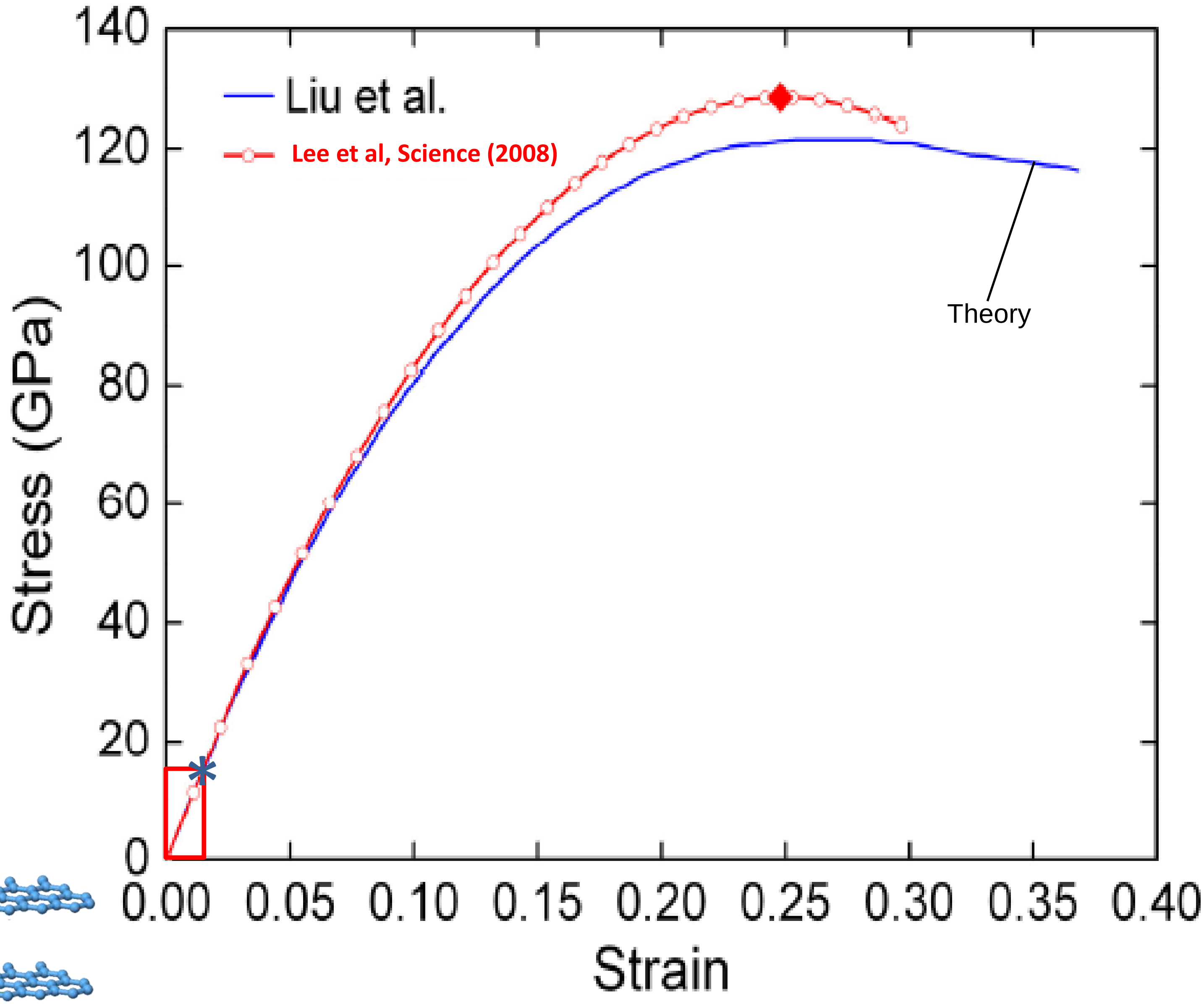
Tsoukleri et al. *Small* **2009**, 5, 2397]

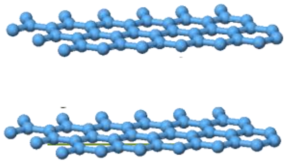
2D Band for embedded flake



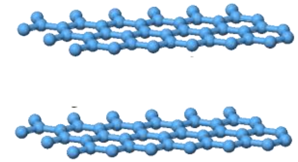
Tsoukleri et al. *Small* **2009**, 5, 2397

Tensile testsin graphene – Current status





Graphene: a powerful stress/ strain sensor



Phonon stress (σ) or strain (ε) sensitivities:

$$\left(\frac{\partial \overline{G}}{\partial \varepsilon}\right)_T \sim -27.0\ (\mathrm{cm}^{-1}\%^{-1}) \rightarrow \left(\frac{\partial \overline{G}}{\partial \sigma}\right)_T \sim -2.7\ (\mathrm{cm}^{-1}\mathrm{GPa}^{-1})$$

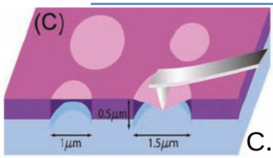
For small(??) strains $\sigma = E\varepsilon, \quad E = 1\,\mathrm{TPa}$ [Lee et al, Science (2008)]

$$\left(\frac{\partial (2D)}{\partial \varepsilon}\right)_T \sim -60.0\ \mathrm{cm}^{-1}(\mathrm{cm}^{-1}\%^{-1}) \rightarrow \left(\frac{\partial (2D)}{\partial \sigma}\right)_T \sim -6.0\ (\mathrm{cm}^{-1}\mathrm{GPa}^{-1})$$

Knowing the wavenumber shift we can resolve the inverse problem i.e. to obtain the values of axial σ and/or ε in graphene-based materials through the above relations.

Frank, O. *et al.* Development of a universal stress sensor for graphene and carbon fibres. *Nat Commun* **2**, 255 (2011).

Mechanical characterization of single layer graphene

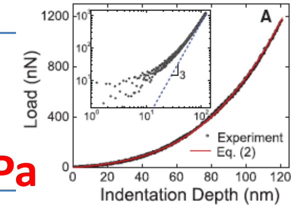


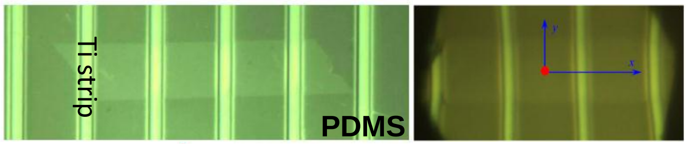
AFM nanoindentation

C. Lee, *et al.*, Science **321**, 385 (2008)

$$F = \sigma_0^{2D}(\pi a)\left(\frac{\delta}{a}\right) + E^{2D}(q^3 a)\left(\frac{\delta}{a}\right)^3$$

E =1.0 TPa, Fracture strength = 130 GPa

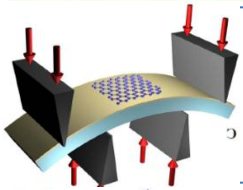




Bending of the substrate (PDMS) & Raman

M. Huang, *et al.*, Proc. Nat. Acad. Sci. **106**, 7304 (2009)

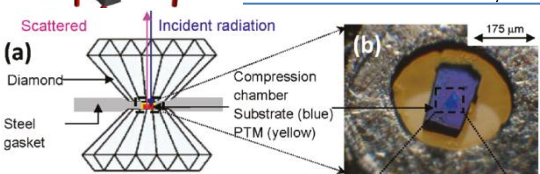
$$\partial\omega_{G^+}/\partial\varepsilon = -12.5\ \mathrm{cm}^{-1}/\%$$
$$\partial\omega_{G^-}/\partial\varepsilon = -5.6\ \mathrm{cm}^{-1}/\%$$
$$\partial\omega_{2D}/\partial\varepsilon = -21.0\ \mathrm{cm}^{-1}/\%$$



4-point bending of the substrate (PMMA) & Raman

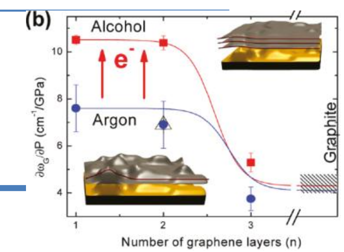
T. M. G. Mohiuddin, *et al.*, Phys. Rev. B **79**, 205433 (2009)

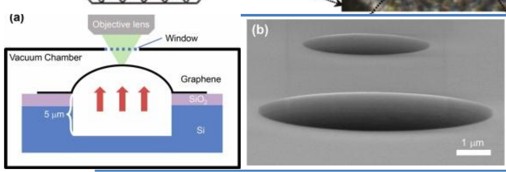
$$\partial\omega_G^+/\partial\varepsilon \sim -10.8\ \mathrm{cm}^{-1}/\%$$
$$\partial\omega_G^-/\partial\varepsilon \sim -31.7\ \mathrm{cm}^{-1}/\%$$
$$\partial\omega_{2D}/\partial\varepsilon \sim -64\mathrm{cm}^{-1}/\%$$



Graphene under pressure & Raman

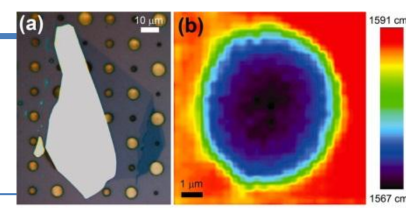
J. Nicolle, et al., Nano Lett. **11**, 3564 (2011)



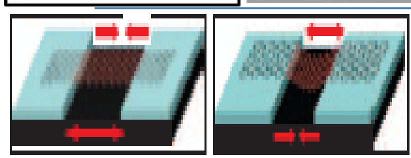


Bulge test & Raman (Biaxial deformation)

J.-U. Lee, *et al.*, Nano Lett. **12**, 4444 (2012)

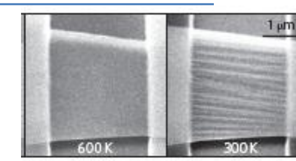


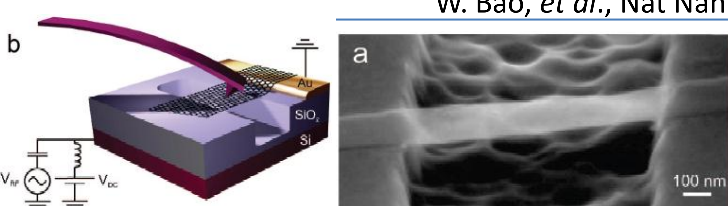
E = 2.4 TPa!!!



Controlled creation of periodic ripples in suspended graphene sheets using **thermally generated strains**

W. Bao, *et al.*, Nat Nano **4**, 562 (2009)

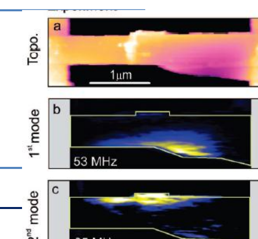




Imaging of a vibrating graphene beam using SPM

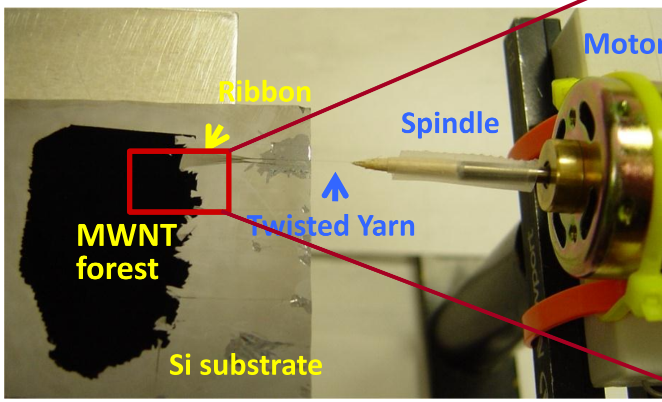
<u>Graphene resonator with local buckling</u>

Garcia-Sanchez, et al., *Nano Lett.*, **8**, 1399 (2008)

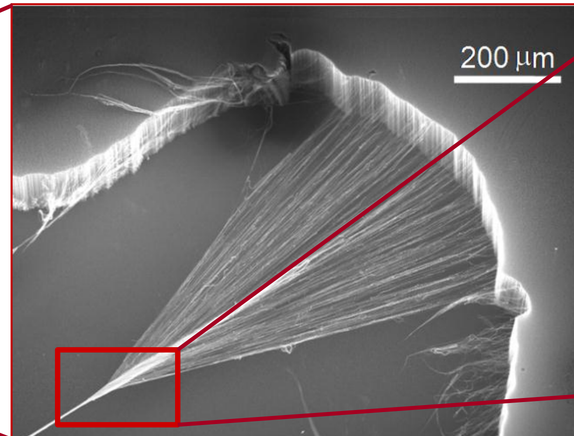


Axial Experiments in CNT yarns
(tension combined with Raman measurements)

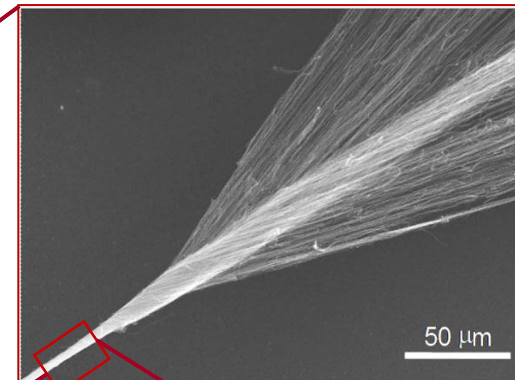
Draw-Twist process for CNT yarn production



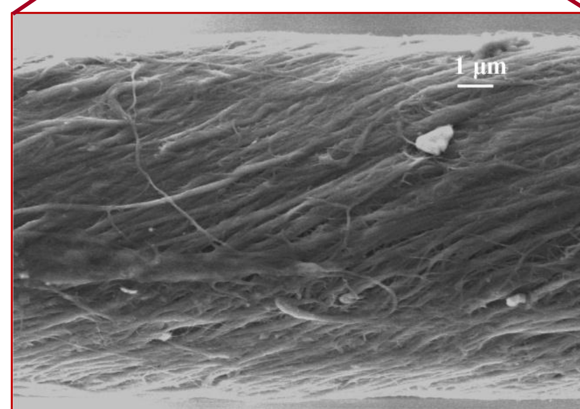
Spinning machine



CNT forest

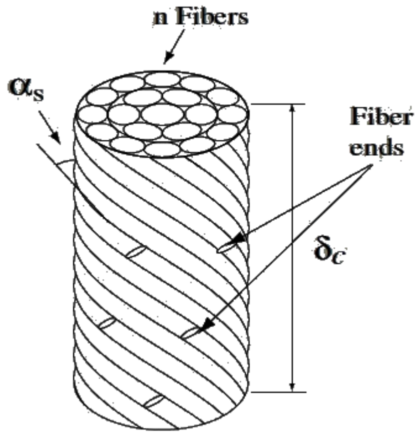


CNT yarn

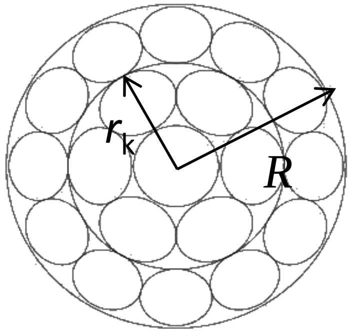


M. Zhang, et al.“*Multifunctional Carbon Nanotube Yarns by Downsizing an Ancient Tecnology”*, Science, **36**, p. 1358, 2004

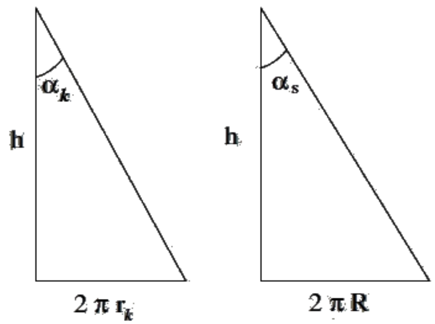
Yarn model geometry (Ideal helical structure)



Yarn segment



concentric packing of *l* layers



layer helix angles

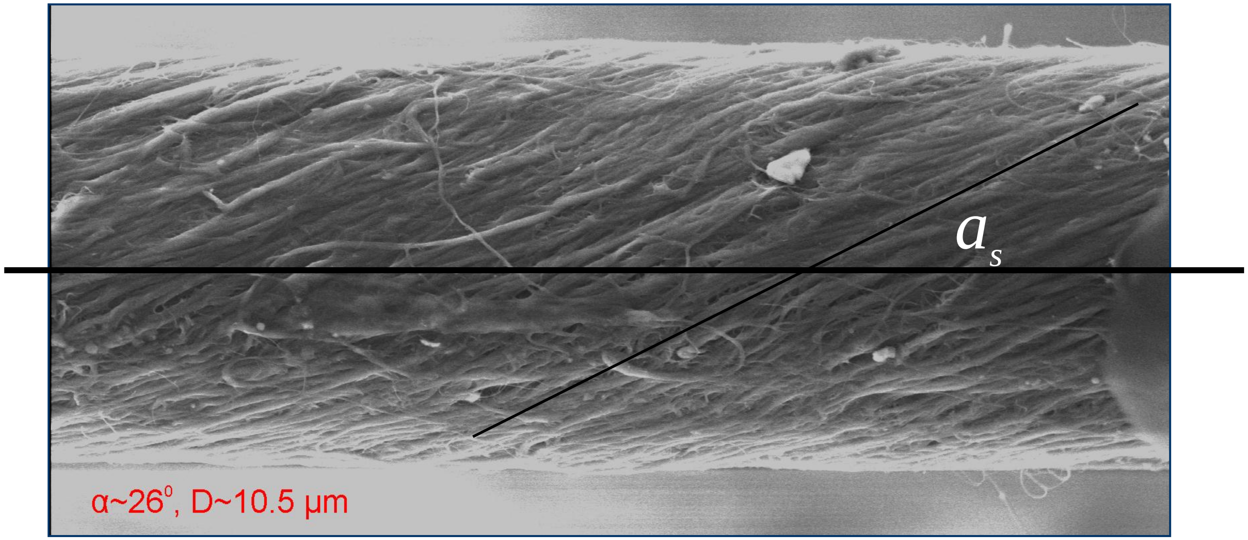
(h is the height along the yarn axis of one turn of twist)

(R is the radius of the outer layer of the yarn and r_k is the radius of layer k)

- Outer layer helix angle $$a_s = \arctan\left(\frac{2\pi R}{h}\right)$$
- Inner layer *k* helix angle $$a_s = \arctan\left(\frac{r_k \tan a_s}{R}\right)$$

Twist (turns/m) of yarns

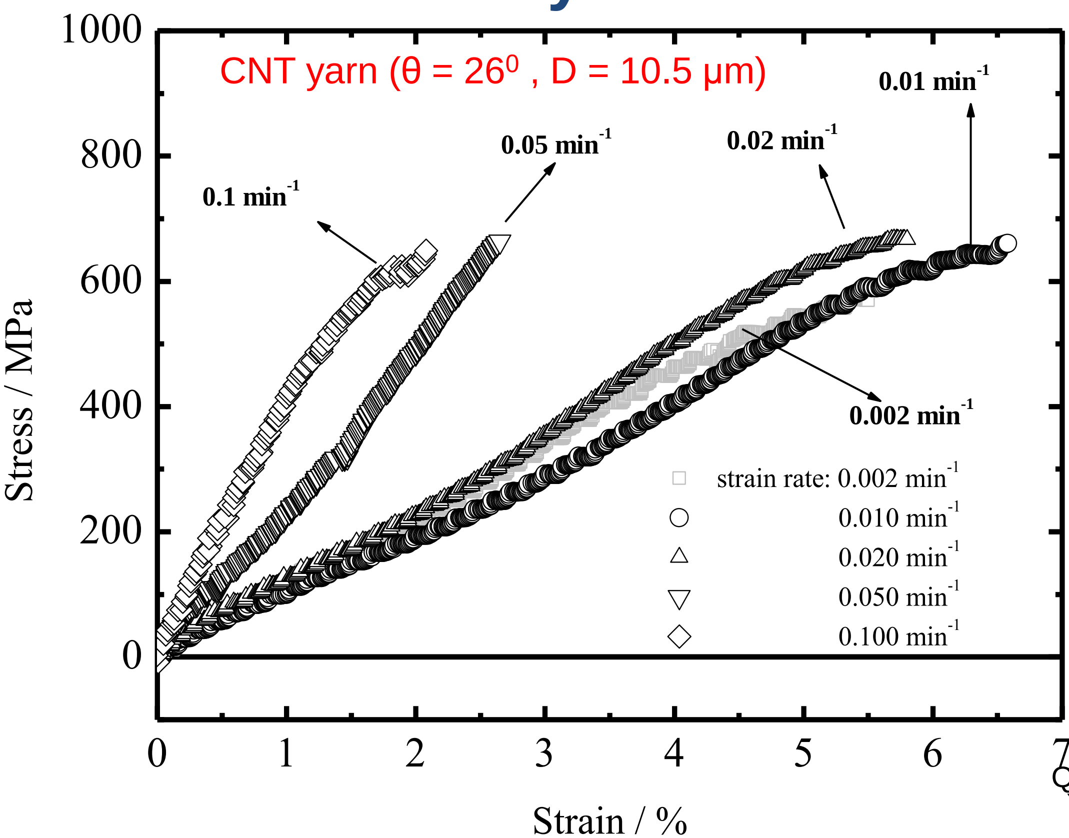
$$\frac{1}{h}=\frac{\tan a_s}{\pi D}$$



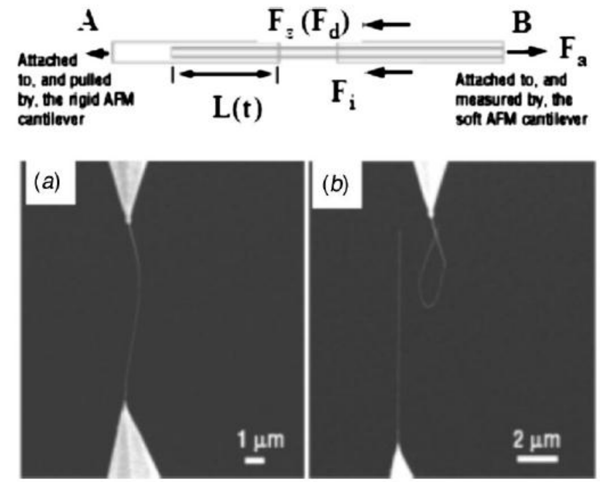
$$a_s=\arctan\left(\frac{2\pi R}{h}\right)\rightarrow\frac{1}{h}\sim 14786\ \mathrm{m}^{-1}$$

where $\alpha_s = 26^o$ and D = 10.5 μm were measured by SEM pictures

CNT yarn mechanical performance



Shell Sliding Experiment in MWCNT

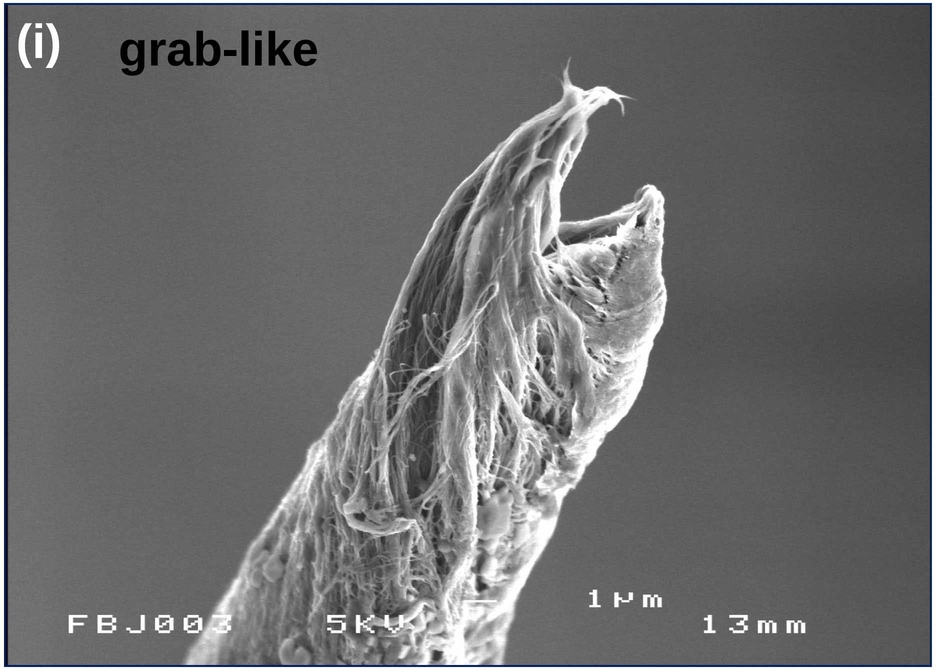


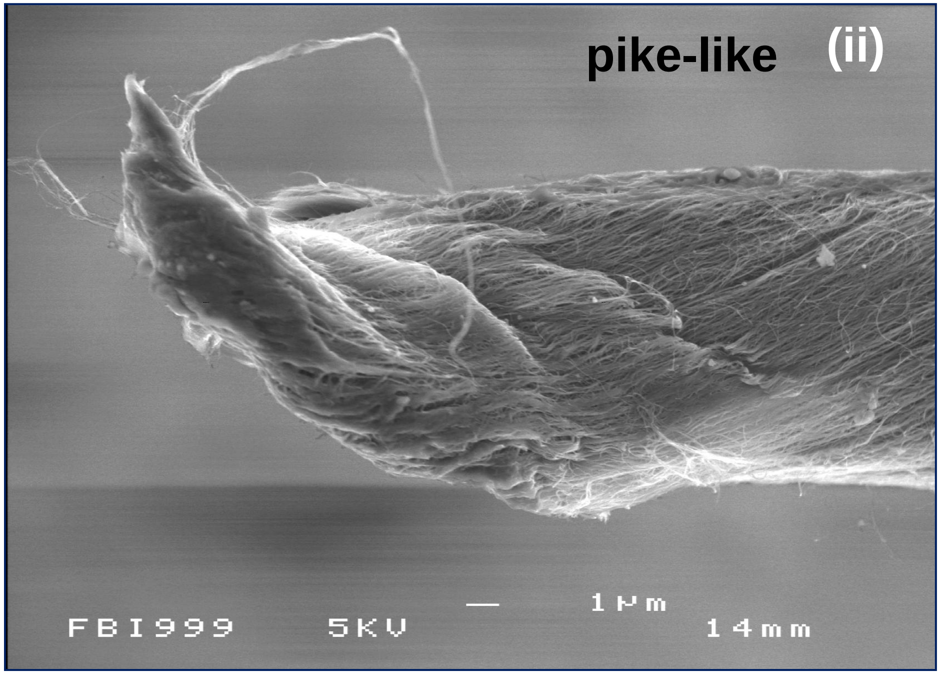
F_a ~ 100-200 nN
shear strength ~ 0.08 MPa

Qian D. eta al. Appl Mech Rev vol 55, no 6, November 2002
Yu, M.-F., et al., . *J. Phys. Chem. B* **104**, 8764–8767 (2000).

- CNT yarns behave like a viscoelastic Material
- Strain-to-failure increases with strain rate
- **CNT yarn strength is 620 MPa and is independent from strain rate**
- **(friction forces are independent from the rate of the relative**
- **movement between CNT bundles)**

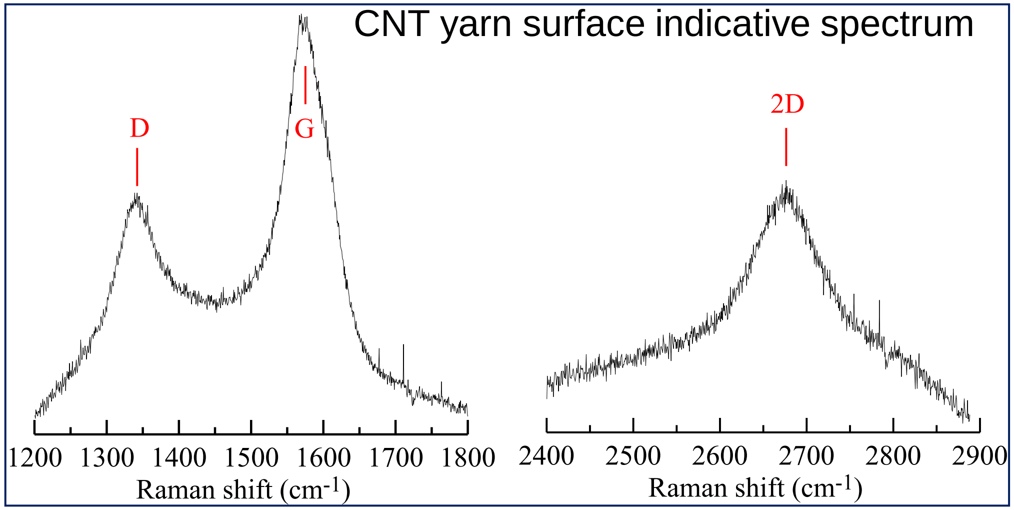
CNT yarn fracture surface





A bundle of MWCNTs located at the yarn centre is clearly unveiled (ii) showing that the bundle is subjected to higher strains when an external tensile load is applied to the yarn. This is consistent with ideal helix yarn models where when an ideal helical structure is under an external tensile load, **the fiber strains are largest along the yarn axis and smallest in the outermost layer**.

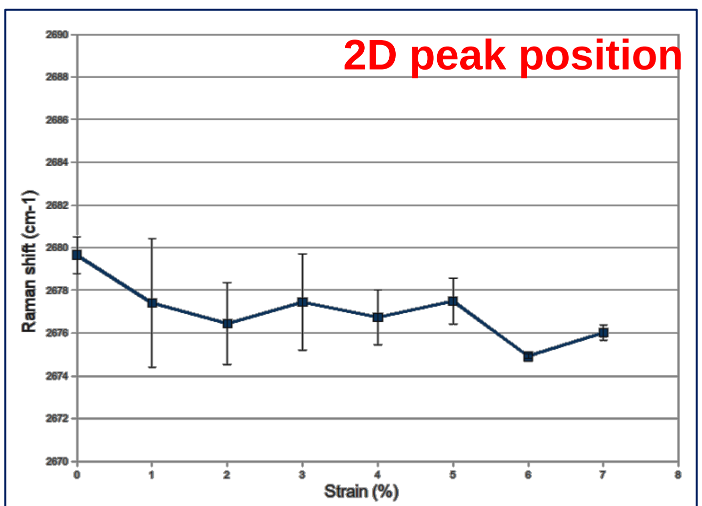
Stress transfer in CNT yarns – Raman Spectroscopy

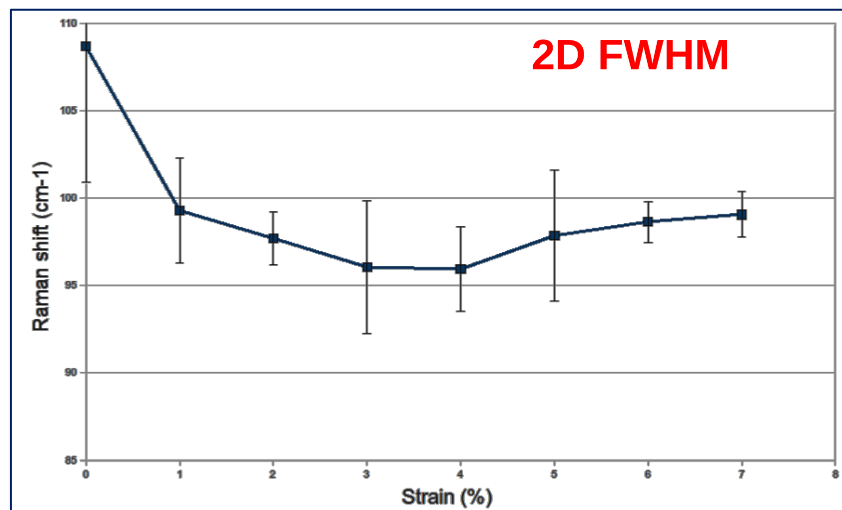


- 2D peak position decreases slightly (~4cm^{-1}) with strain
- 2D FWHM decreases showing a min value which reflects the decreasing of helix angle and consequently the spread of strain values

These results indicate that **the fiber strains are largest along the yarn axis and smallest in the outermost layer.**

2D peak position and FWHM as a function of **uniaxial tensile strain**

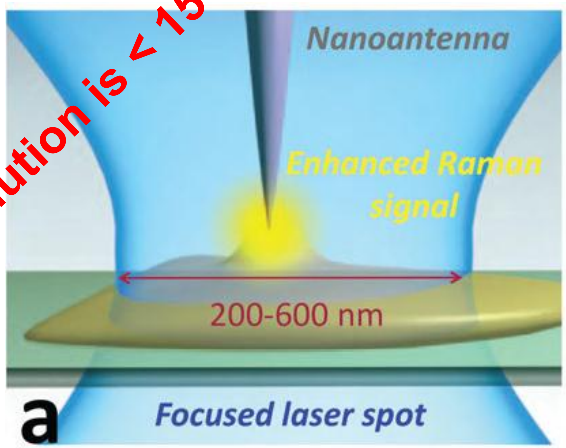


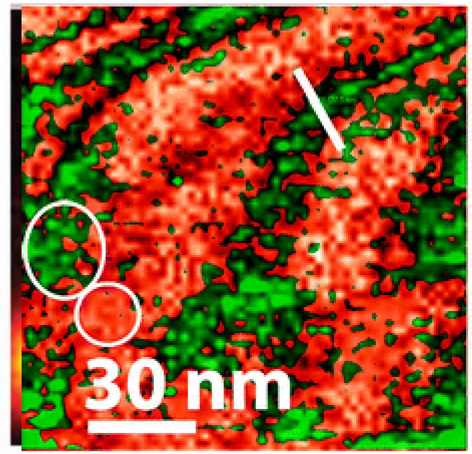


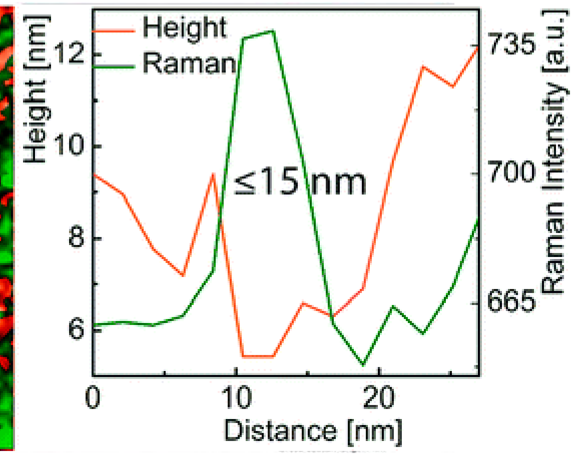
Breaking the diffraction limit with TERS (Tip Enhanced Raman Spectrocopy)

AFM + Raman microscopy

lateral resolution is < 15 nm!!!!

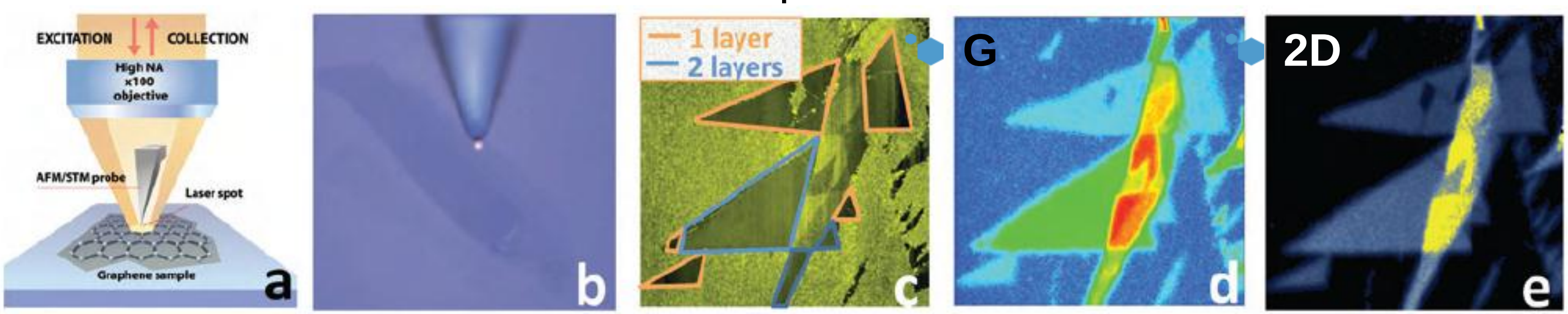






Graphene

Stadler, J., et al., Nano Lett. 10, 4514–4520 (2010).



The AFM nano-antenna can locally enhance the electromagnetic field intensity near the tip apex and become a localized “nano-source of light.”

P. Dorozhkin et al, Microscopy Today, doi:10.1017/S1551929510000982 (2010)

Thank you very much for your kind attention !