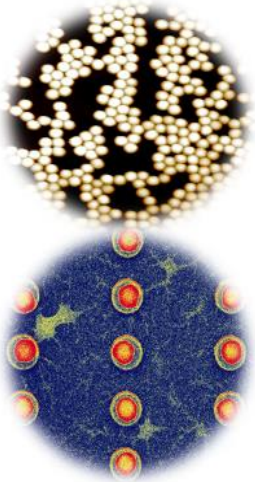
Accelerated Mechanical Property Mapping and High-Resolution Chemical Mapping/Spectroscopy

Gajendra Shekhawat
Research Professor
Department of Mat. Sci. & Eng.
SPID Manager, NU*ANCE* Center
Northwestern University

Dimension ICON AFM System

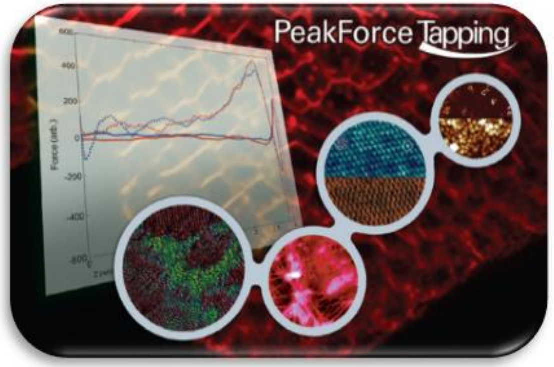


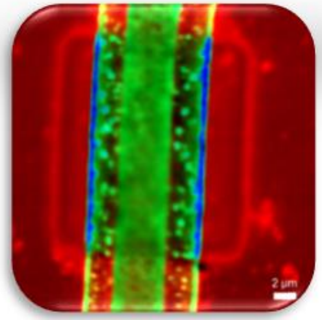
High Speed AFM System


32 Hz scan rate with peak force tapping and scan Assyst Mode.


1fr/sec at 256 pixel, automated measurements

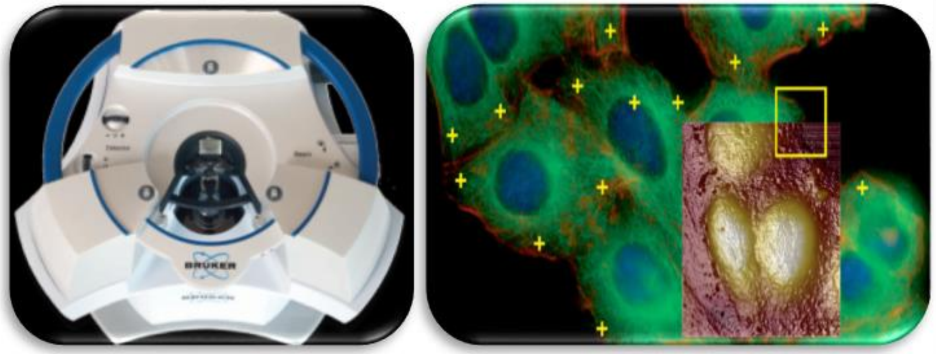

Automated laser and detector alignments



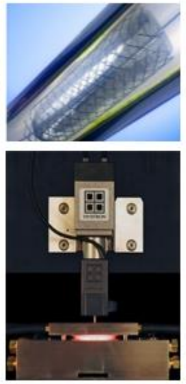


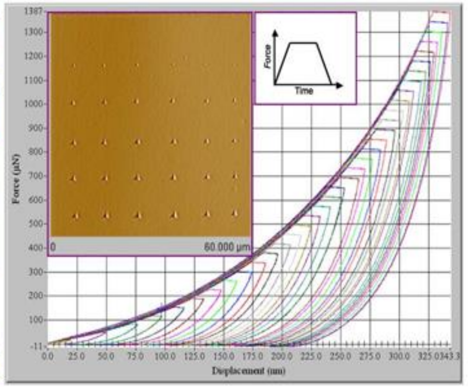
🟥 cSi, 🟩 polySi, 🟦 ncSi

Raman Spectrometer



Life Science Imaging System

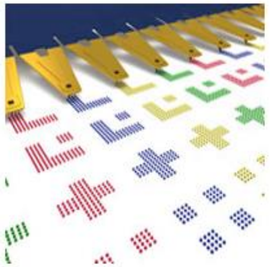




Nanomechanical Analysis Hard Materials

Biosoft Indenter

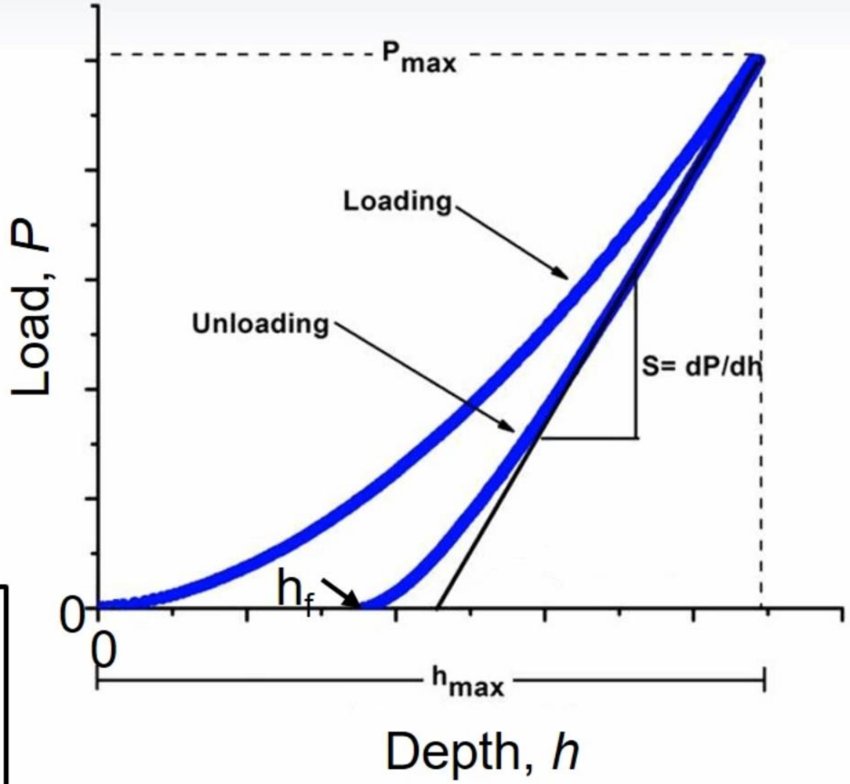
Biomaterials nanopatterning capabilities

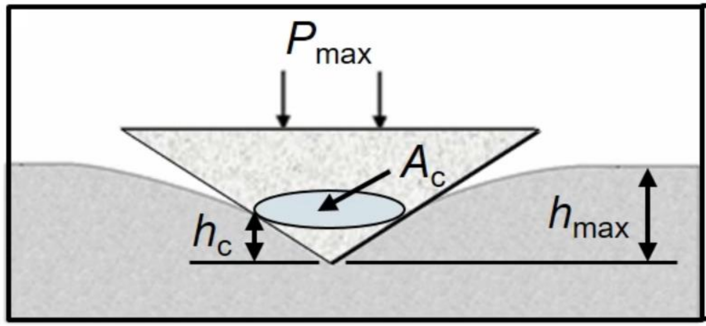


Quasi Static Indentation
Dynamic Mechanical Analyzer
Feedback Control Displacement
Modulus Mapping
SPM Imaging
Temperature Control
Complete Automation

Basic Nanoindentation Principles –
Quasi-Static Nanoindentation

- Depth sensing technique– constant acquisition of load and depth
- Contact area fit using calibration against a standard sample – Variety of probe shapes can be used
- Main extracted properties – hardness and modulus



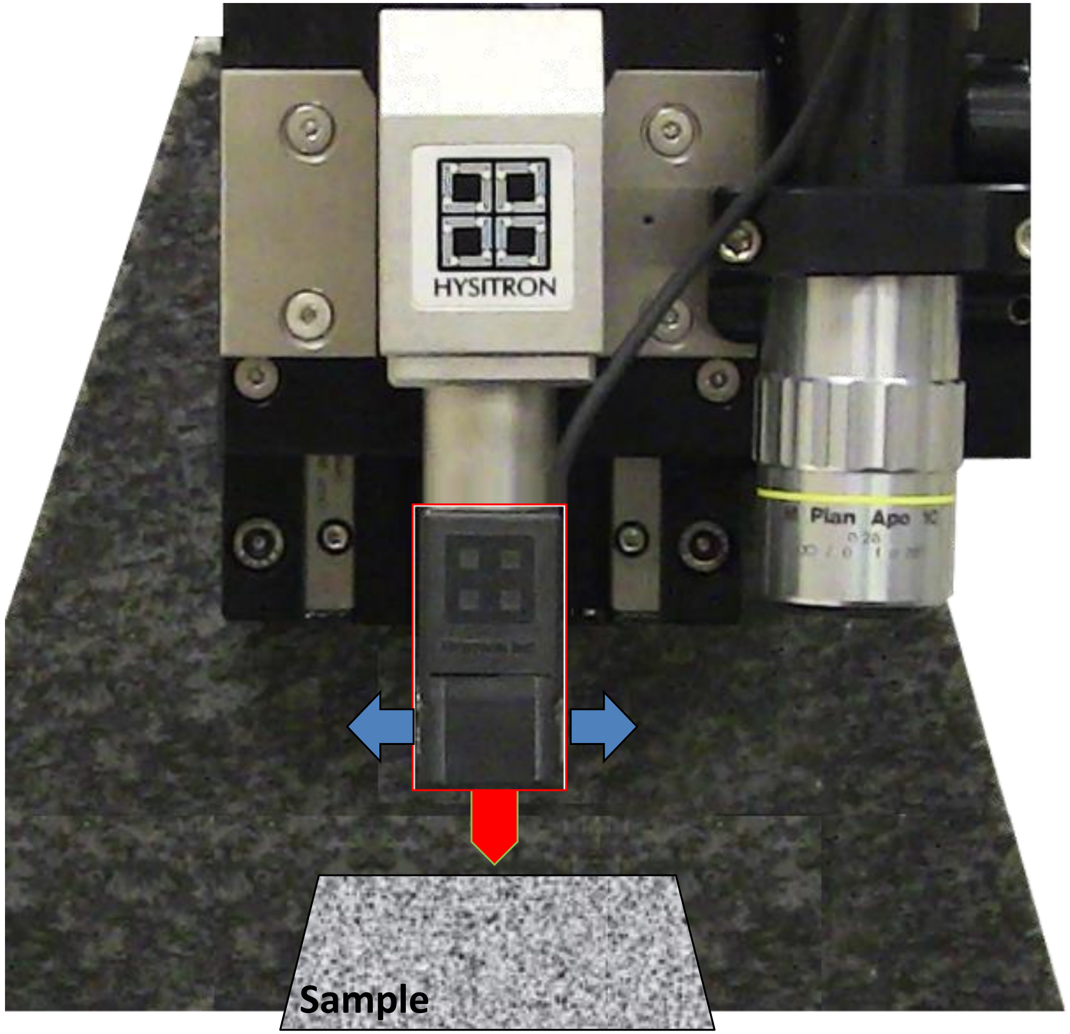


Elastic Modulus (*E*) **Hardness (*H*)**

$$E_r = \frac{S\sqrt{\pi}}{2\sqrt{A_c}}$$

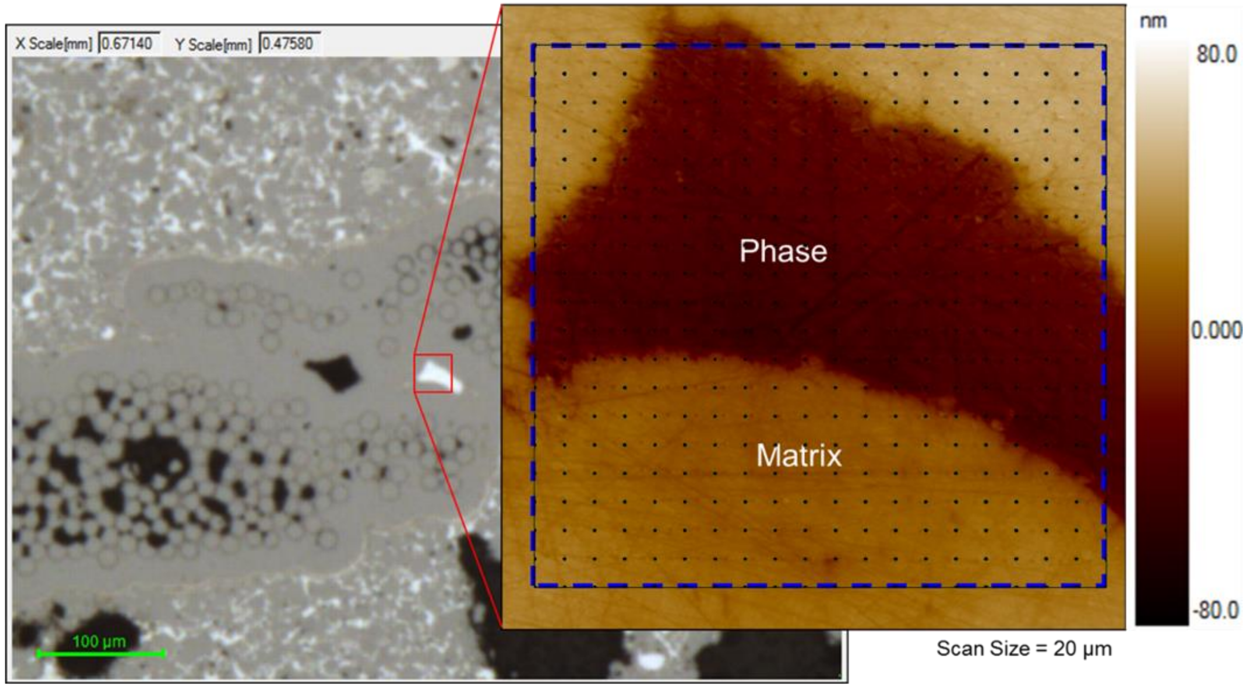
$$H = \frac{P_{\max}}{A_c}$$

Large Arrays of Indents at 6 indents/s

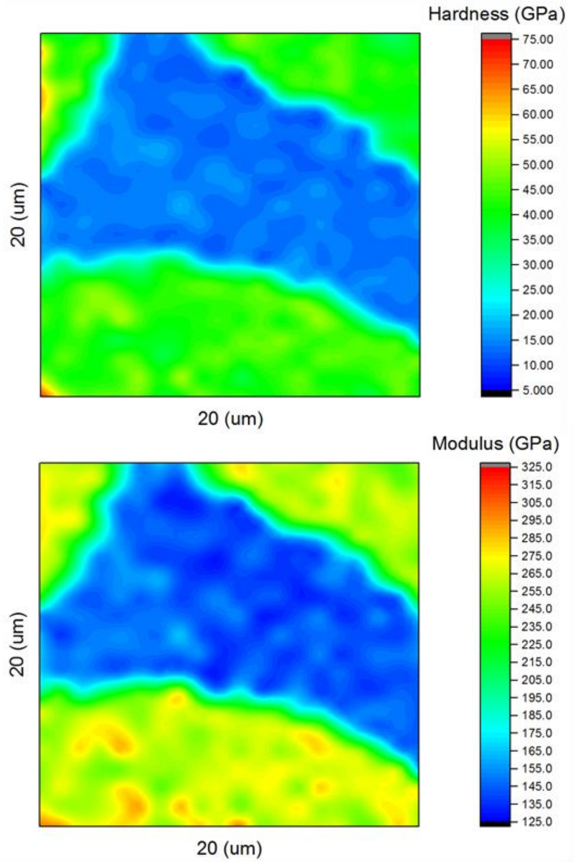


- How it works:
  - Approach routine makes contact with the sample
  - Electrostatic actuation to perform experiment and withdraw
  - Between indents, piezo is moved to next position
- TI-980: up to 18ms / indent
- Minimizes;
  - Drift
  - Probe wear
  - Sample changes due to operando conditions

XPM High Resolution Property Mapping



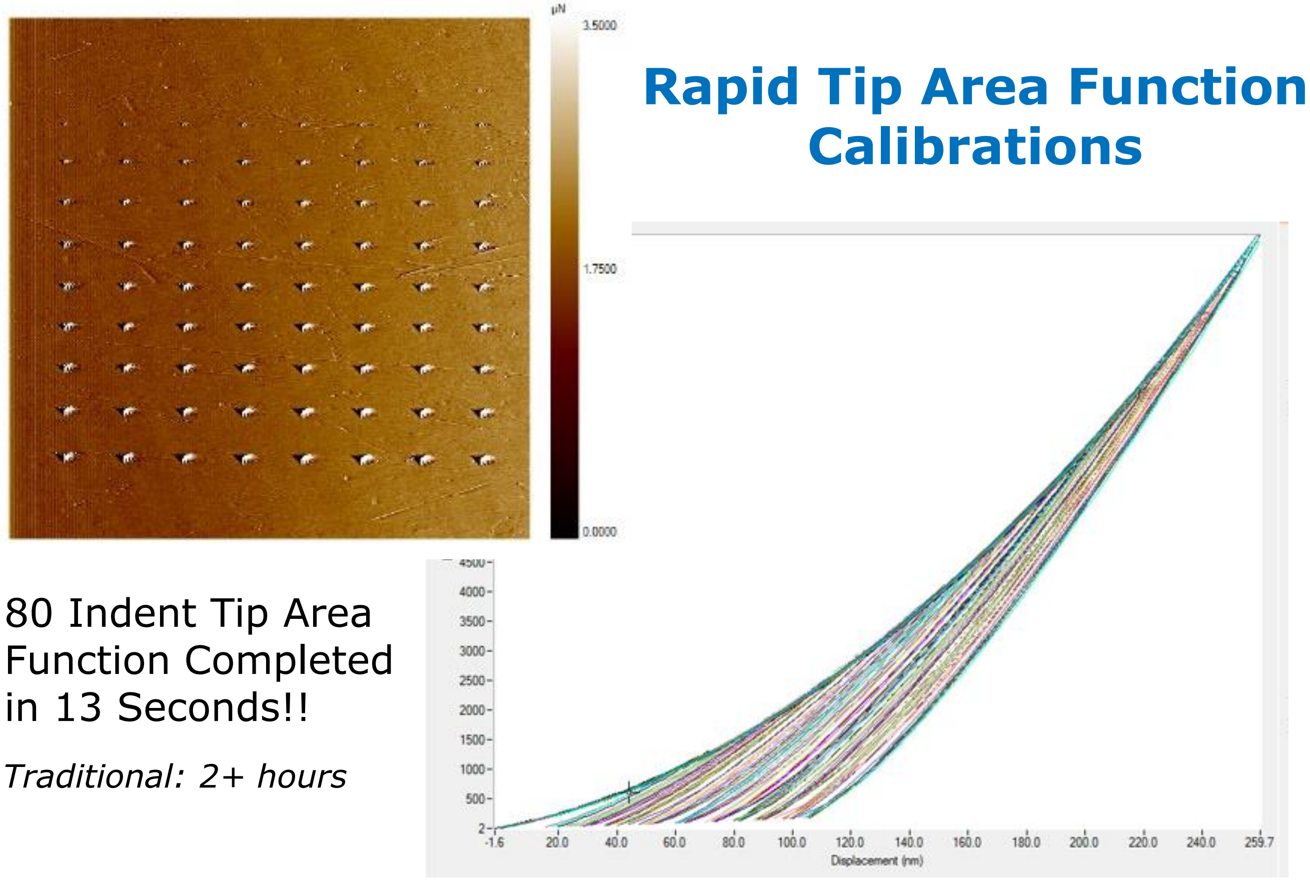
400 Measurement Array (20x20)
on a Ceramics Matrix Composite.



XPM - High Speed Nanoindentation

6 Nanoindentation Measurements/Second

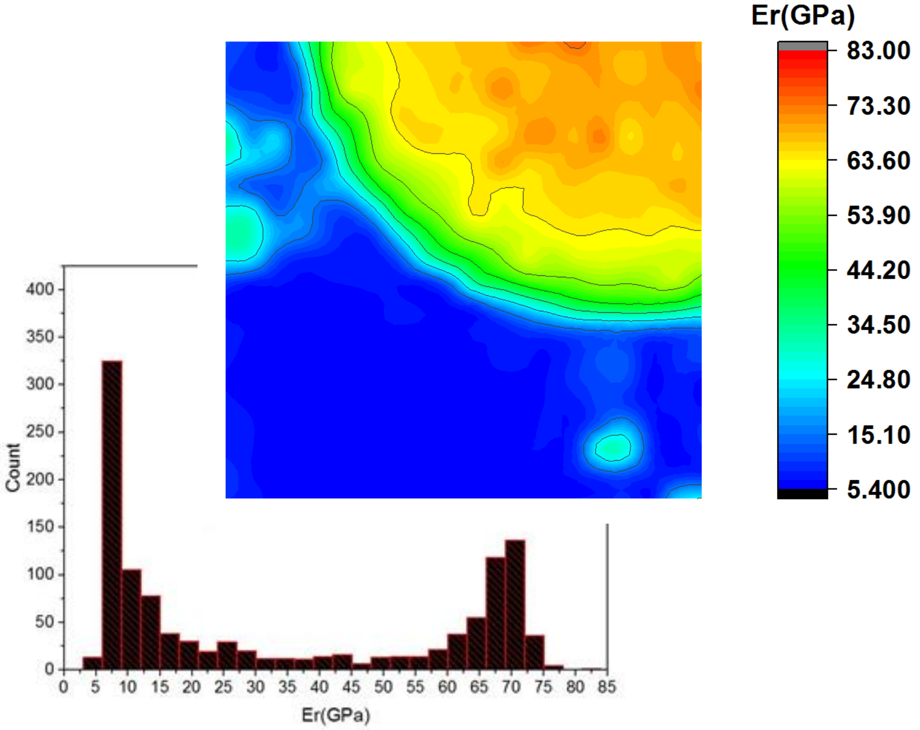
Rapid Tip Area Function Calibrations



80 Indent Tip Area Function Completed in 13 Seconds!!

Traditional: 2+ hours

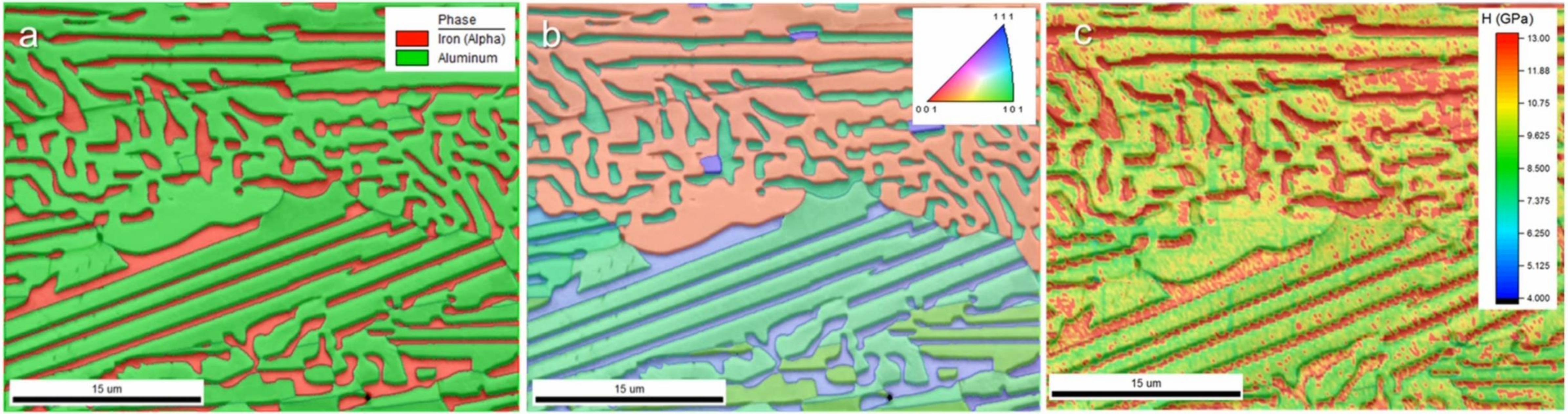
Fast Property Mapping with Distribution Statistics



More data in a single afternoon than you could have previously taken in a year!

Fine Microstructure Mapping

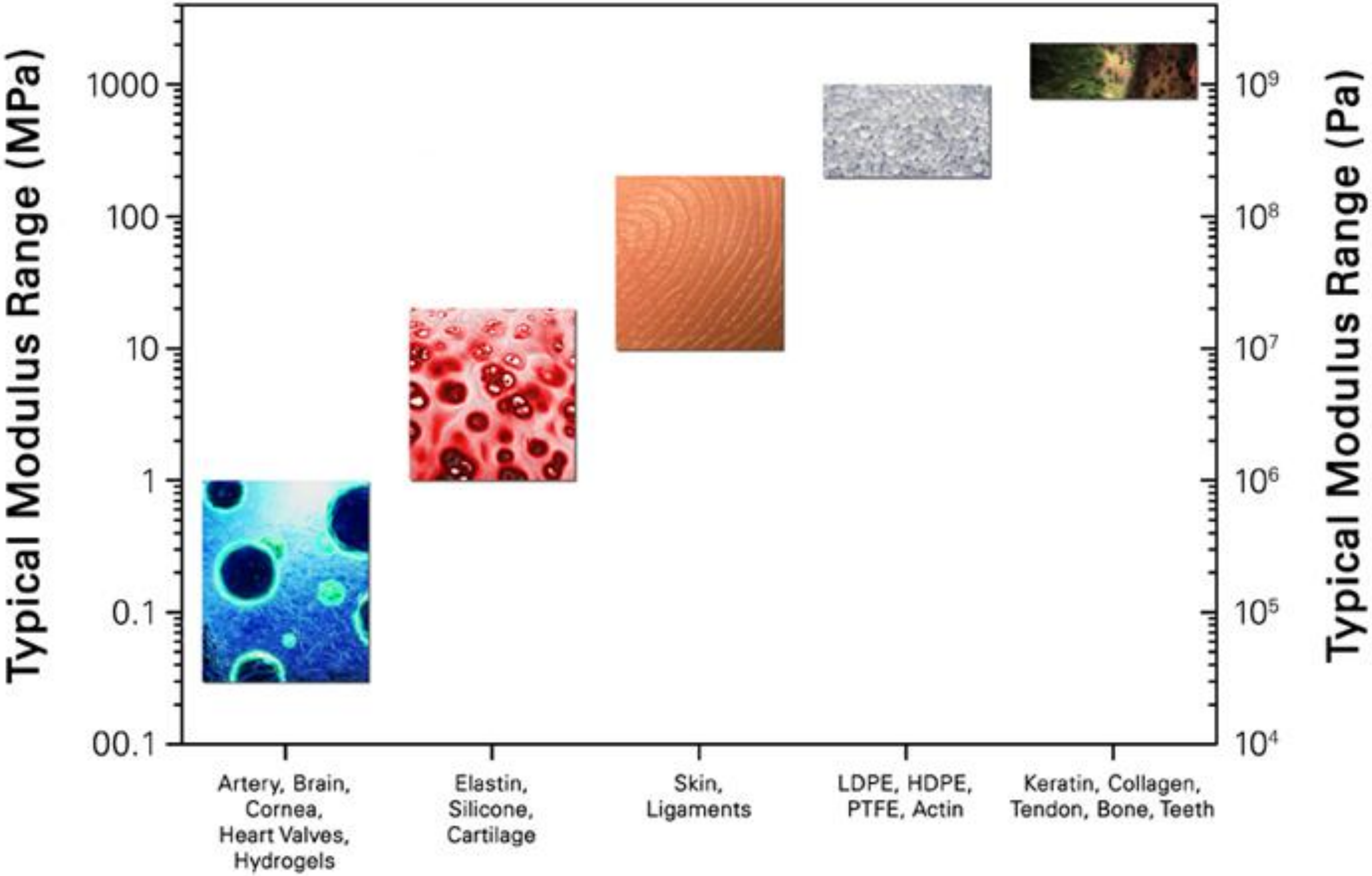
xProbe™ XPM – 0.1 µm Resolution (same as EBSD)



EBSD Phase Map EBSD Inverse Pole Figure Map XPM Hardness Map

Biomatter Modulus

Characterization Spanning 6 Orders of Magnitude

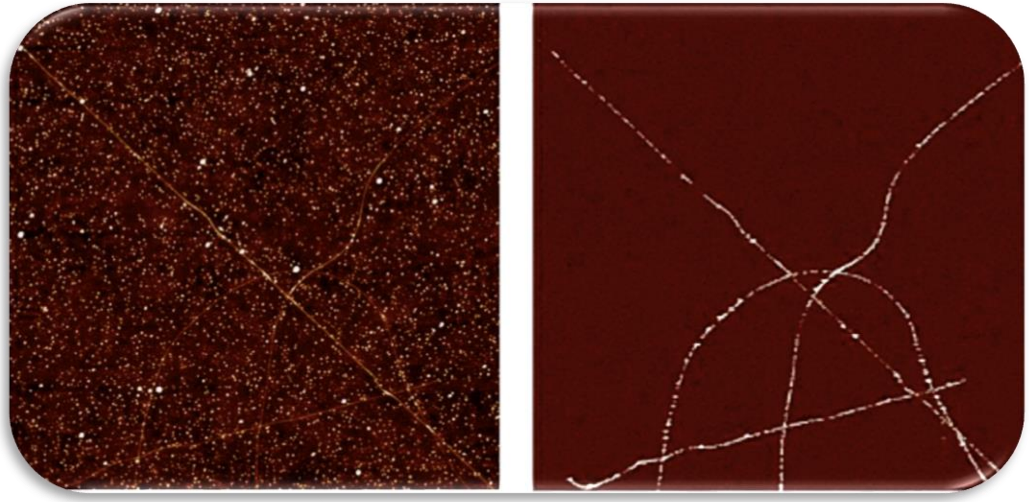


Bringing Scanning Probe Microscopies…

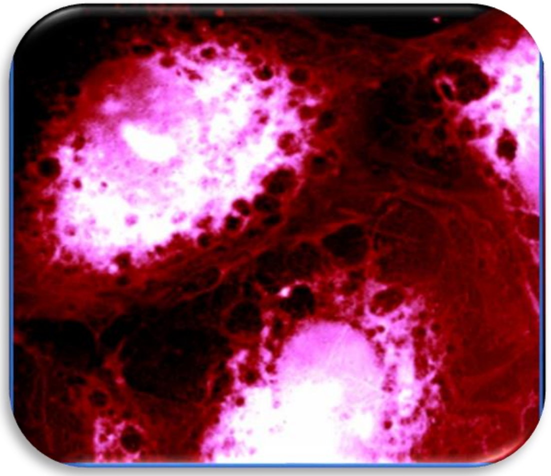
- **SPM** brings a lot of information on the **physical characteristics** of materials
  - *Topography*
  - *Mechanical properties*
  - *Electrical and magnetic properties*

- SPM is truly a nanoscale imaging technique…

…but it lacks ***chemical*** sensitivity



Electrical analysis of carbon nanotubes with electric AFM



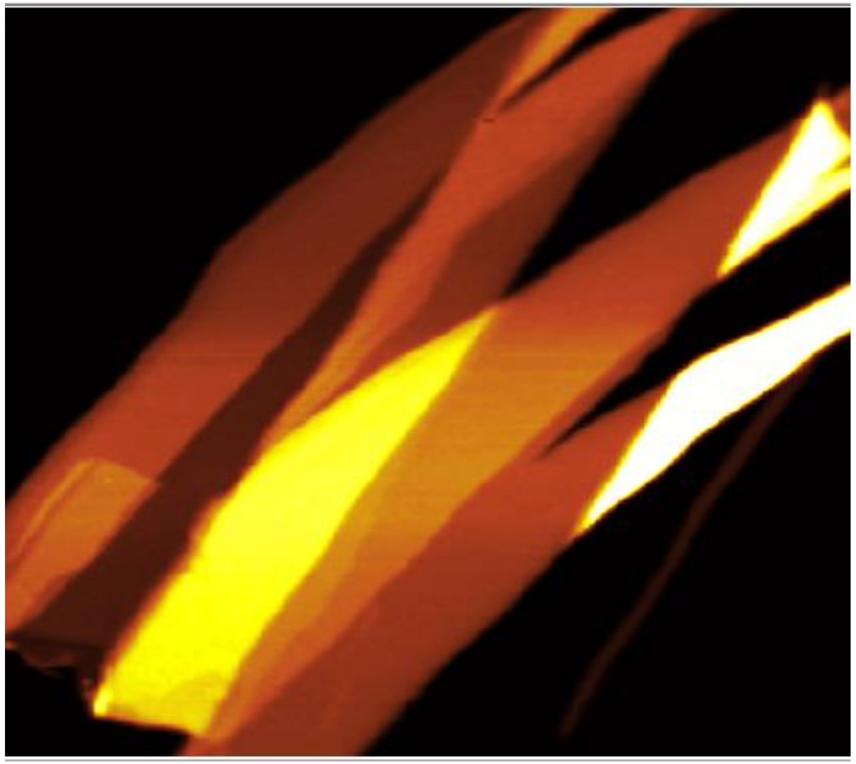
Medulloblastma Cancerous Cells

... and Raman together

- Confocal Raman Microscopy is a very *specific* **chemical imaging**
  - Precise structural information, wide areas of application
  - Non-destructive technique, compatible with many environnements
  - A wide spectrum of available laser sources

  (from UV to IR)

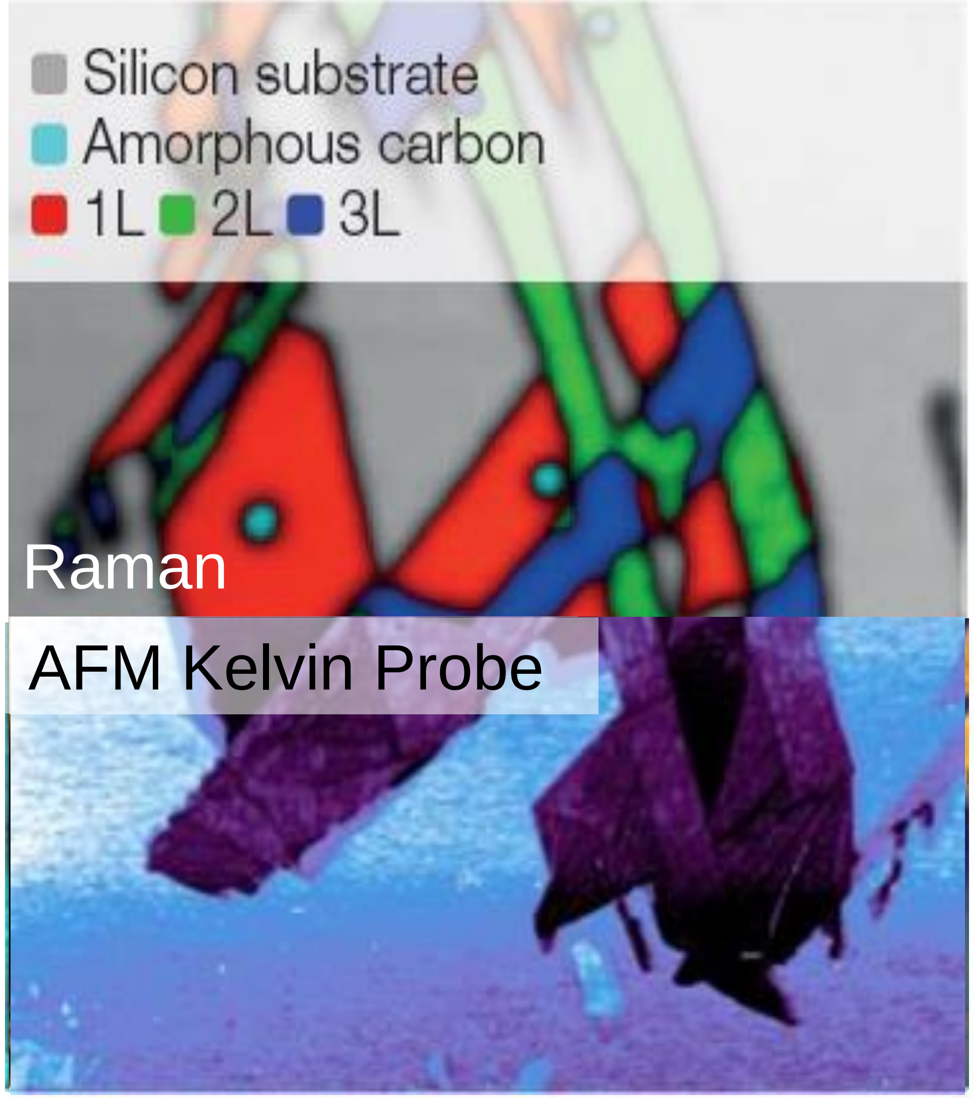
- **Drawbacks**
  - **Low cross-section**
  - **Limited spatial resolution**



Graphene

Bringing AFM together with Raman/PL

Co-localized



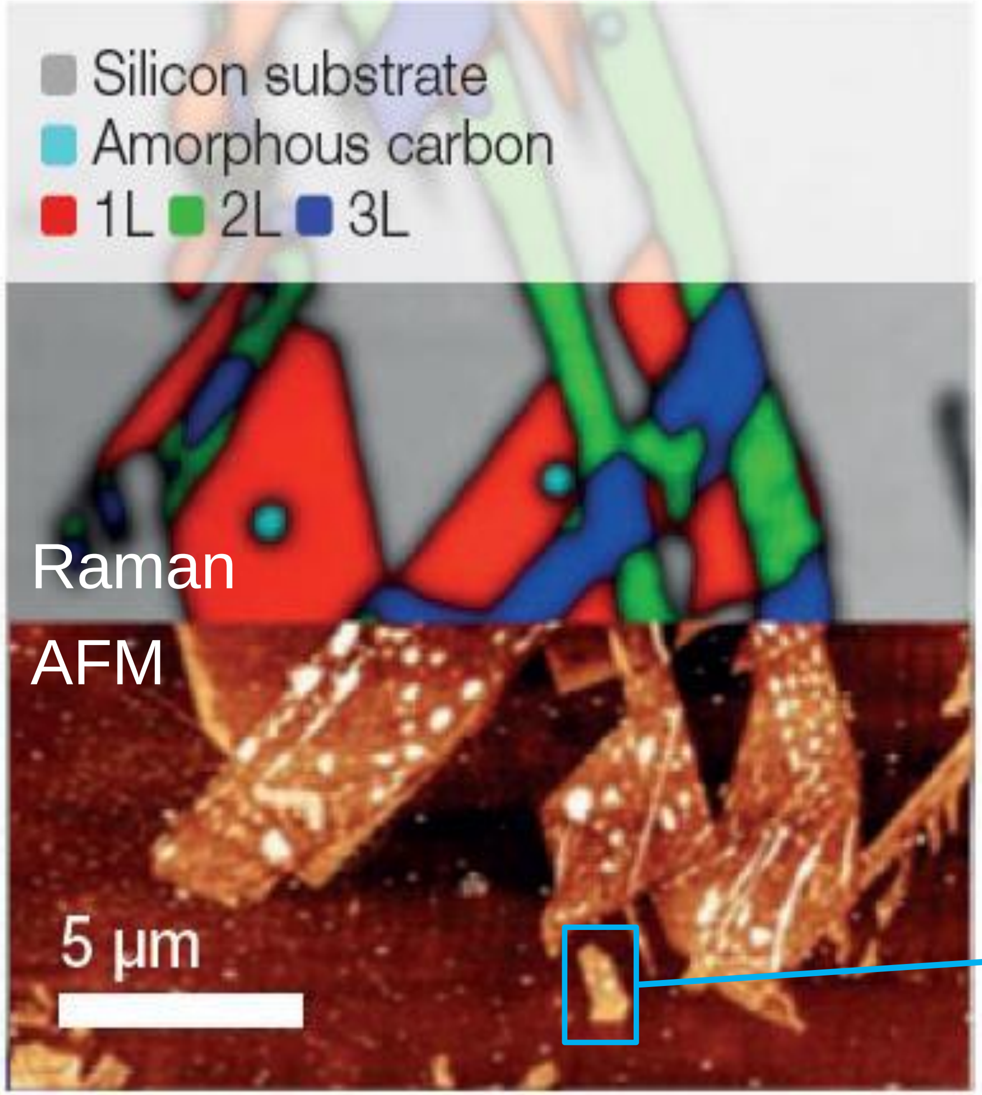
- Chemical
- Topographic
- Mechanical
- Electrical
- Magnetic

etc…

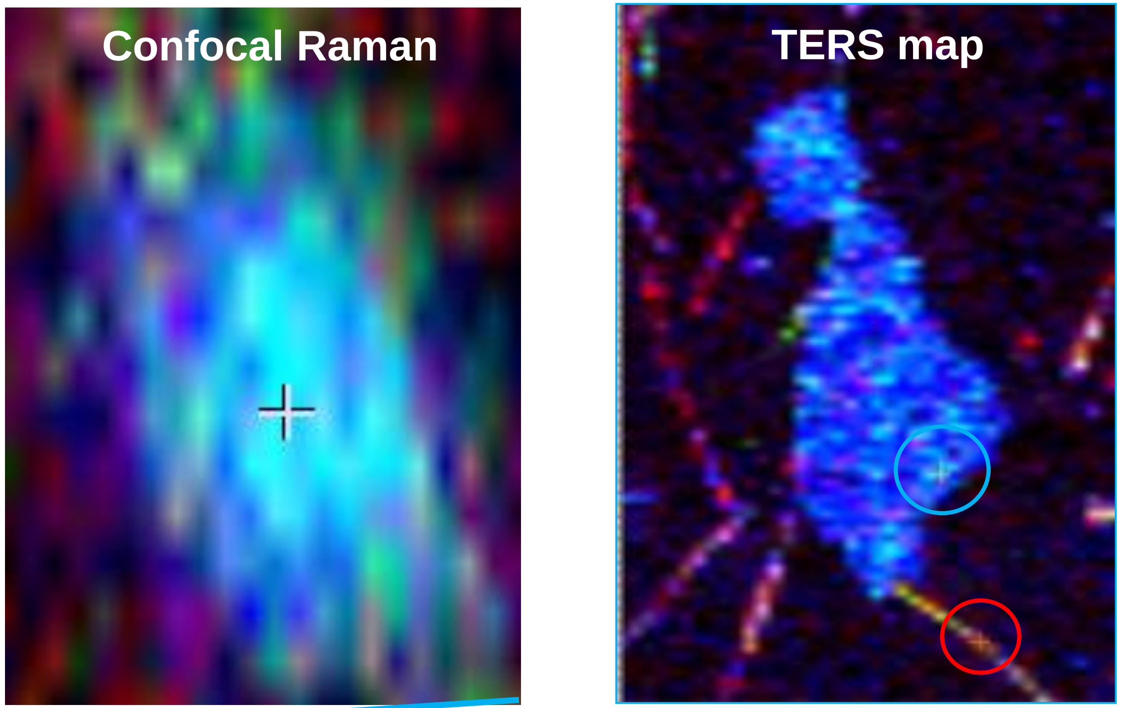
What about the sub-micron features?...

Bringing AFM together with Raman/PL

Co-localized



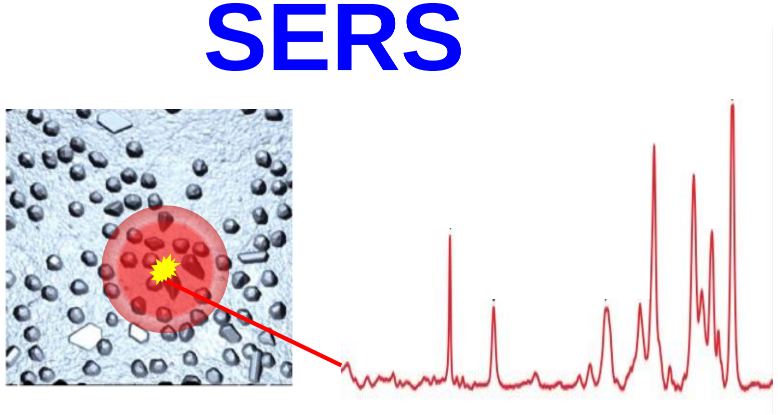
Confocal Raman and TERS of the <u>same area</u>, graphene oxide and CNTs



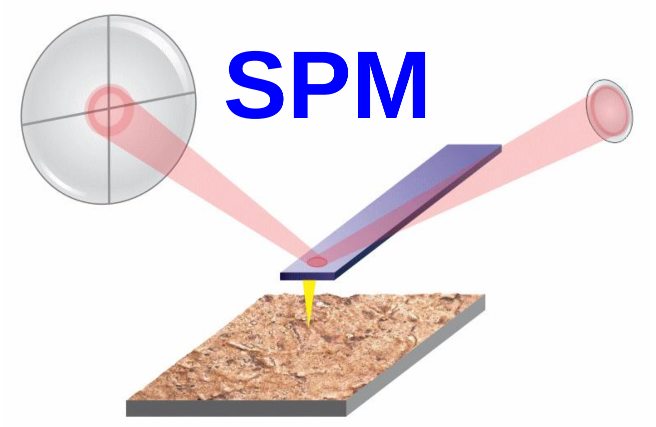
How is it possible?...

Nanoscale heterogeneities- need nanoscale Raman and PL, that's why TERS

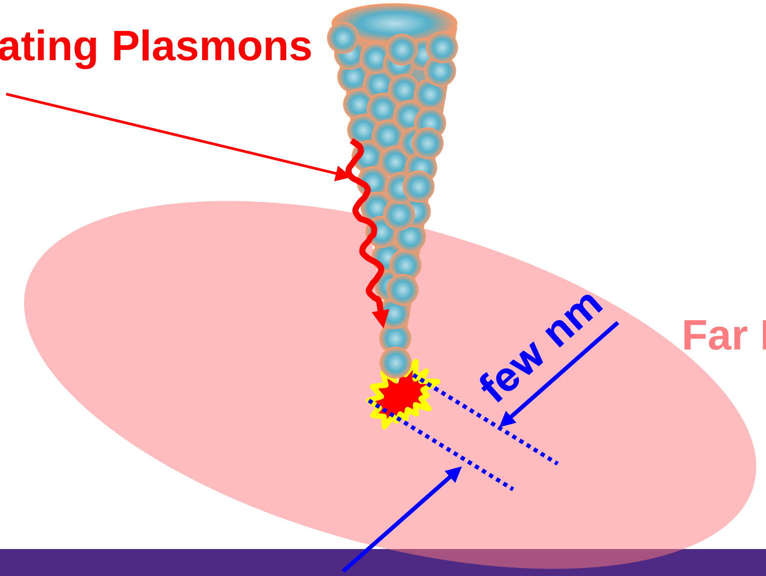
SERS



SPM



TERS



Propagating Plasmons

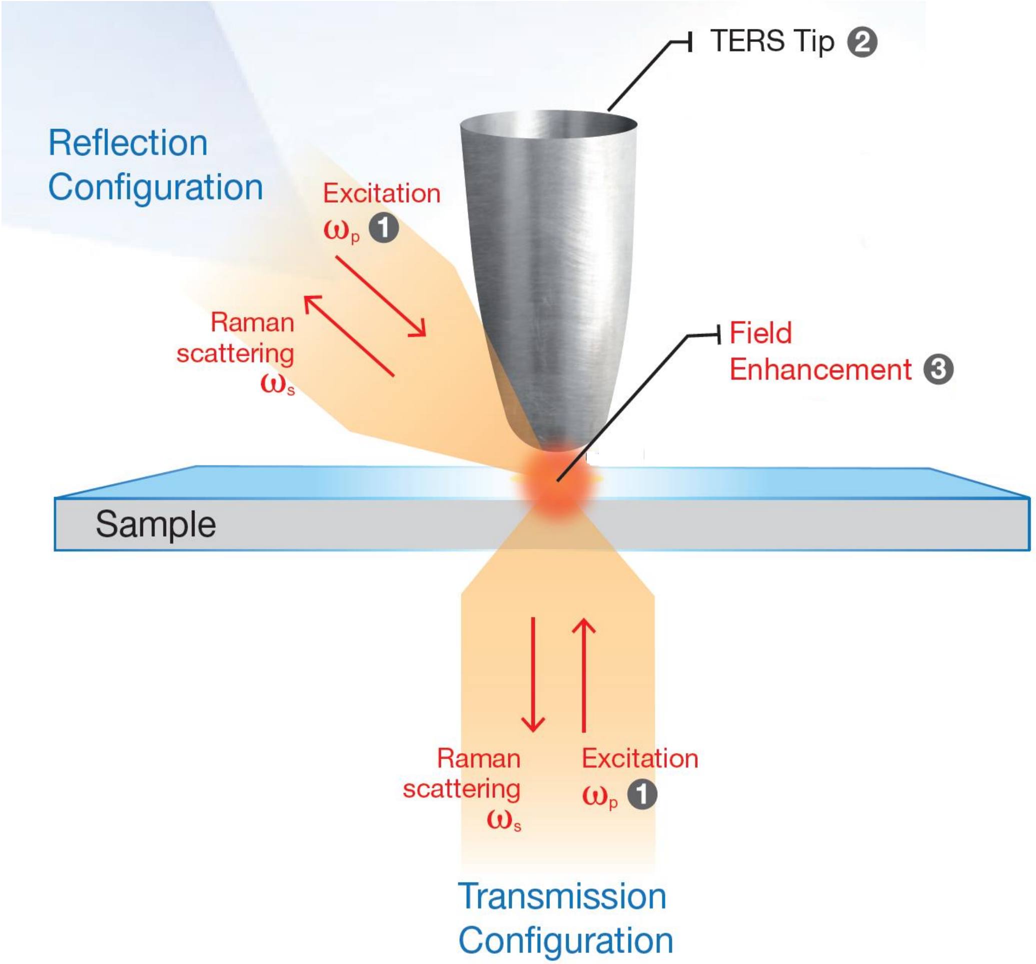
few nm

Far Field Confocal Spot

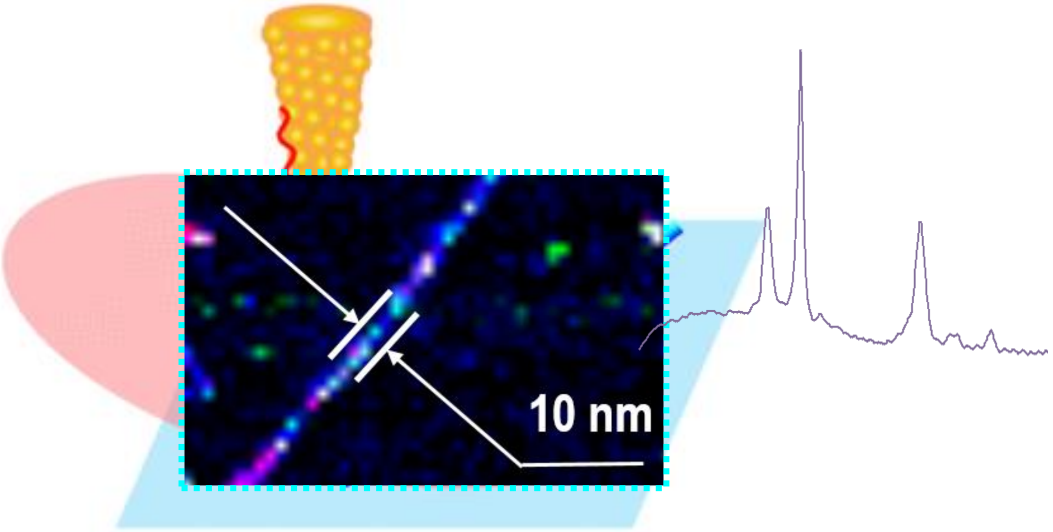
Localized surface plasmon resonance (LSPR):

When the right wavelength of light hits a noble metal surface, the conduction electrons will begin to oscillate with the electric field and in turn amplify the surface electric field. **In combination with Raman spectroscopy, this can amplify the signal by a factor of 10^8 for SERS, 10^6 for TERS**.

Tip-enhanced Raman Spectroscopy (TERS)



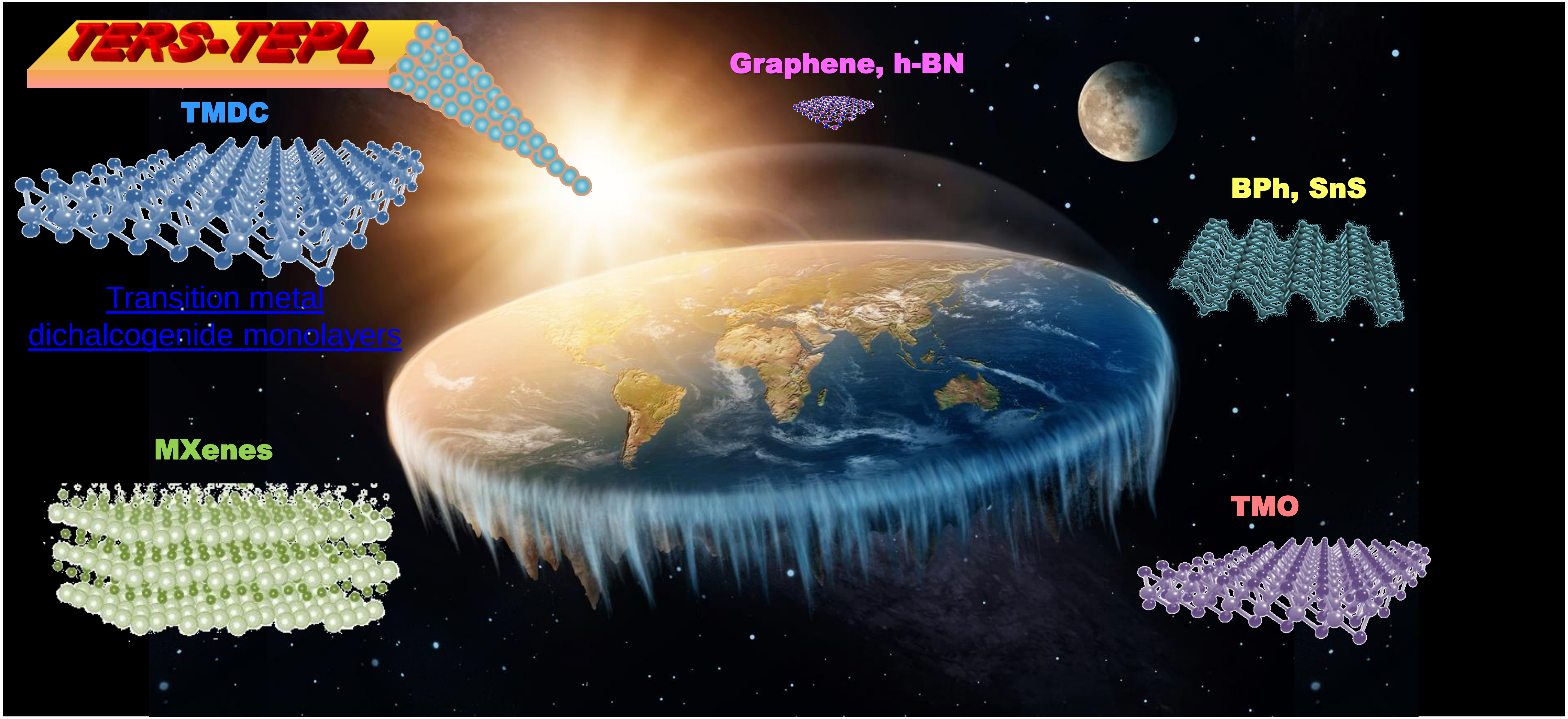
- Combine AFM, Raman, and LSPR effect to get nanoscale spatial resolution and surface analyte detection!
- Confine plasmon resonance effect to nano-sized “hot spot” at tip-sample junction.
- Requires right instrument configuration, noble metal tip and substrate, and very thin (1-2 nm preferable) sample.



Amplification of Raman signal by $10^{5\text{-}7}$ in TERS

J. Phys. Chem. B 110, 6692, 2006
Optics Express 21, 25271, 2013

NanoRaman and NanoPL for the Flatworld



TMDC

[Transition metal dichalcogenide monolayers]

Graphene, h-BN

BPh, SnS

MXenes

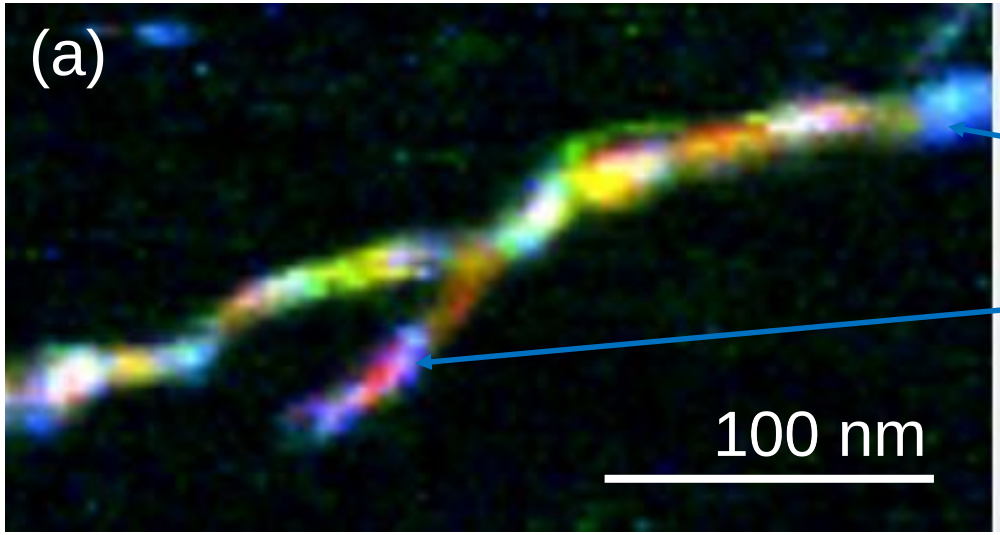
TMO

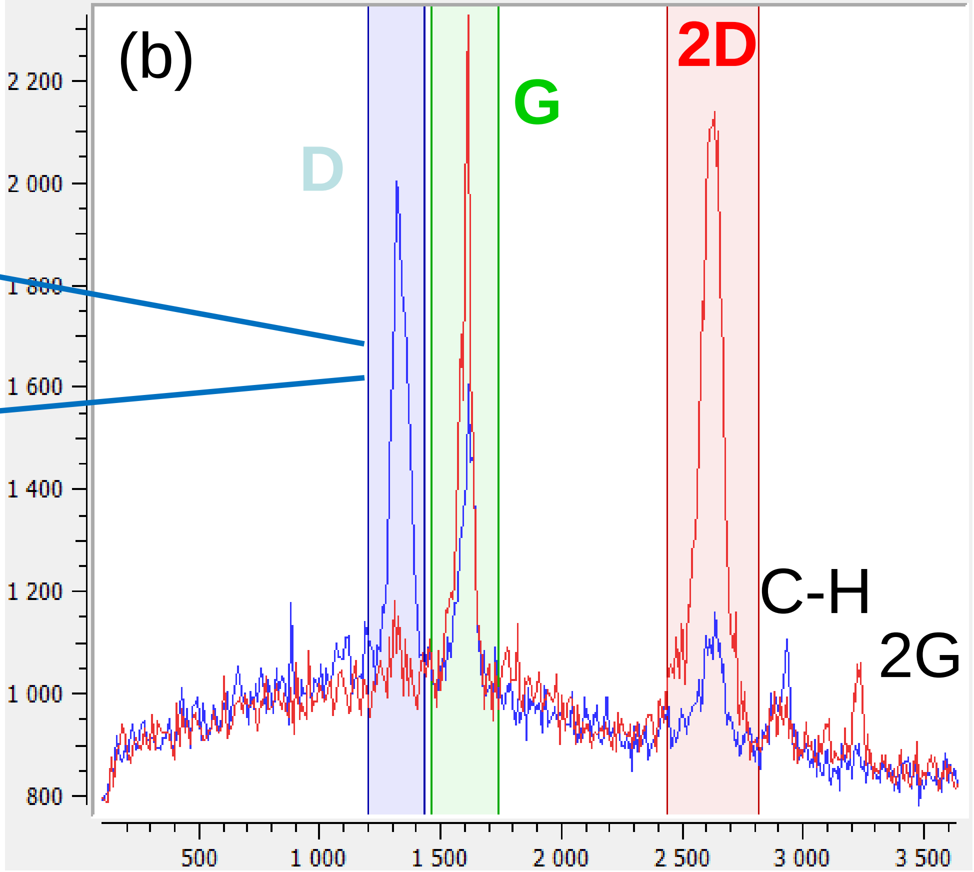
1D materials: Nanotubes and Nanowires

Image Credit: Horiba Inc.

Why TERS? → to characterize **1D materials** in terms of **defect sites**, chirality variations, electronic behaviour

Local defects are seen with TERS (D band)





Chemical mapping of a single nanotube, **TERS acq time/ pixel 100 ms**

a TERS map of a single CNT

b TER spectra of the CNT

Defects density in the structure of CNTs

TERS and TEPL for materials research

AFM provides:
- Topography
- Adhesion / stiffness
- Surface potential
- Conductivity
- Capacitance (charge carrier concentration)
- Photocurrent

Optical spectroscopy:
- Structure, defects (Raman)
- Electronic band structure (PL)
- Mechanical strain (Raman peaks shift)
- Doping (PL and Raman)
- Photocurrent

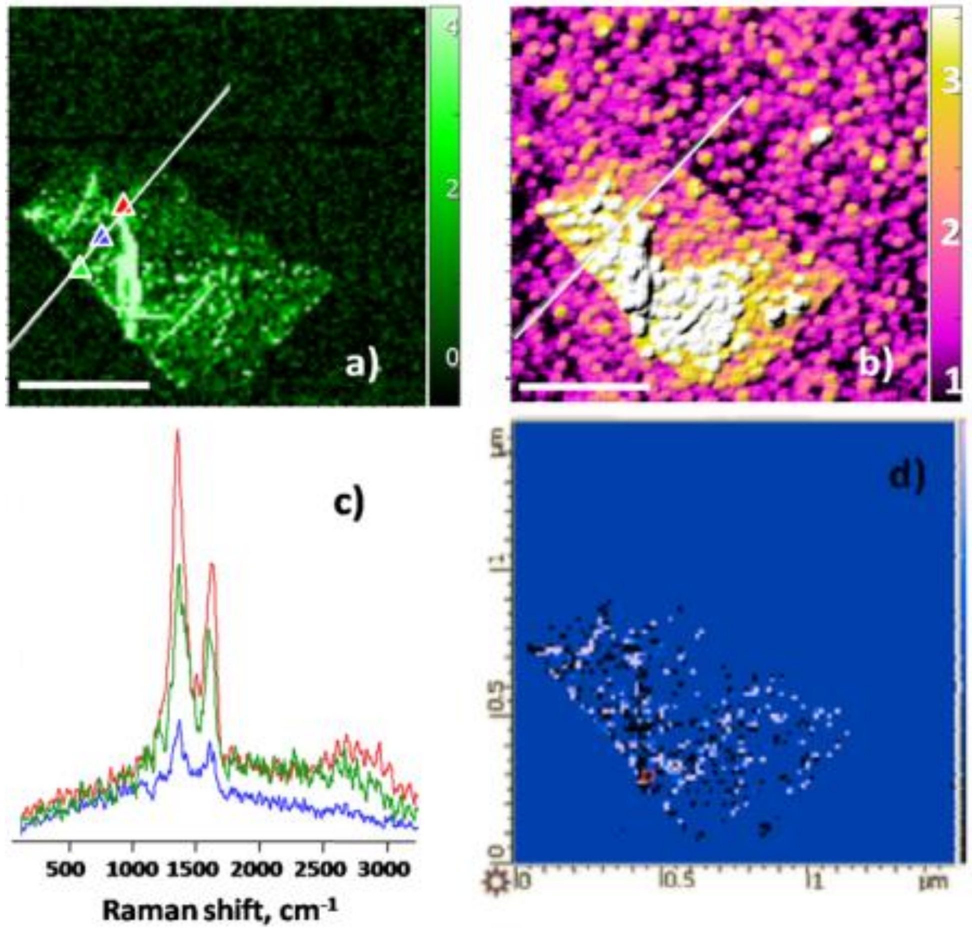
TERS/TEPL

all this at the nanoscale

Available lasers for TERS & TEPL:
532, 473, 633,785, 830 nm

2D materials: Graphene

Why TERS?



a) 100 pixels per line TERS map of D-band intensity, **TERS acq. time/pixel 75 ms**.
b) Topography image of the same flake
c) representative TERS spectra
d) distribution of the ratio of D to G band intensities

The defects density increases with the ratio I_D/I_G

→ Single point defect can be imaged in graphene and graphene oxide flakes with TERS

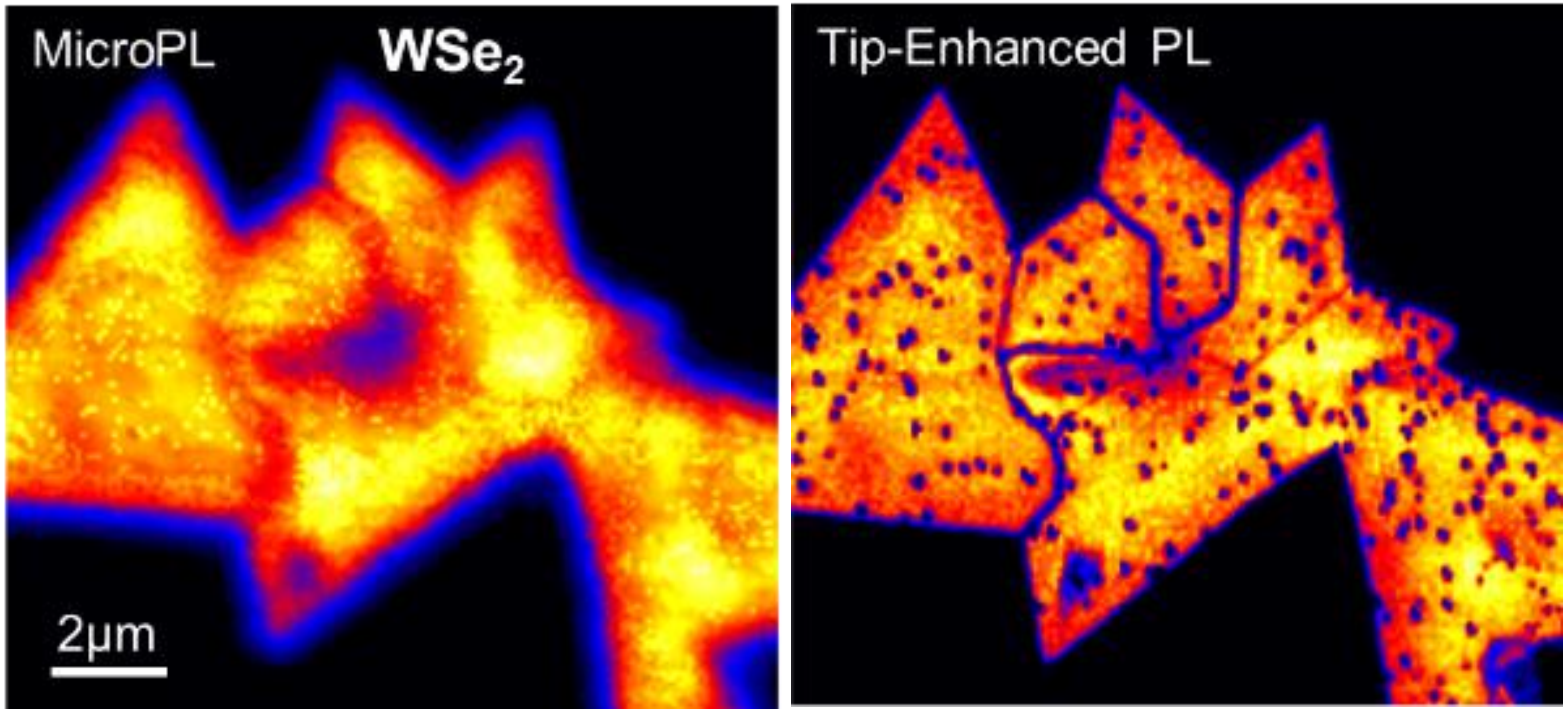
Image Credit: Horiba Inc.

2D materials: TMDC

Image Credit: Horiba Inc.

Why TERS/TEPL?

a.k.a. Far-field PL
(without the tip)



a.k.a. Near-field PL
(with the tip)

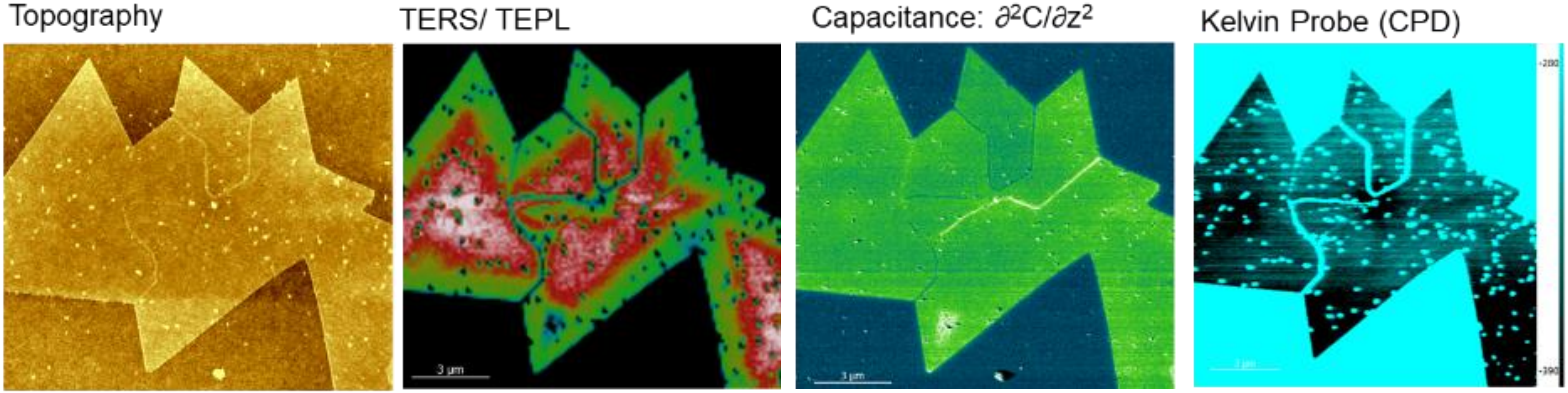
$WSe_2/SiO_2/Si$
TEPL acq. time/pixel: 50 ms

Probing Heterogeneities on 2D TMDCs

point defects, dopants, grain boundaries, edges, wrinkles, strain, presence of nanometric terraces and other nanocrystals, alloys etc

2D materials: TMDC

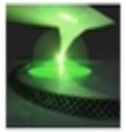
Why TERS? → to **correlate information** (topography, electrical, electronic, and chemical properties) all resolved at the **nanoscale**



$WSe_2/SiO_2/Si$, 17×15 µm, **TERS/TEPL acq. time/pixel: 50 ms**

Image Credit: Horiba Inc.

CONCLUSIONS



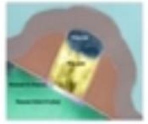
TERS is the combination between sSNOM and Raman; It requires a p-polarized laser, side configuration, noble metal tip.

TERS is done with an AFM-Raman platform. Such systems also allows co-localized AFM-Raman measurements together with all the SPM modes. Thus, both physical (including electrical) and chemical properties of the sample are probed.

The local defects in 1D materials such as CNTs can easily be probed with TERS.

Nanoscale heterogeneities (TERS, TEPL) are revealed on 2D materials (MoS2, MoSe2, WS2); nanometric terraces, grain boundaries, defects, nanocrystals etc. affect the carrier density and thus the optoelectronic properties.
TERS and others SPM modes (KPFM, capacitance etc.) are correlated to link chemical and physical information.

Molecules are also probed with TERS, down to the single molecule sensitivity. Grafting quality, segragation, network can be studied at the nanoscale.



The feasability to measure the mechanical strain in a semiconducting nanostructure at the nanoscale through TERS is demonstrated.

TERS shows that the signature of distinct nucleobases can be detected, opening up opportunities for label-free DNA sequencing. The possibiity to detect single virus with TERS is also mentionned.