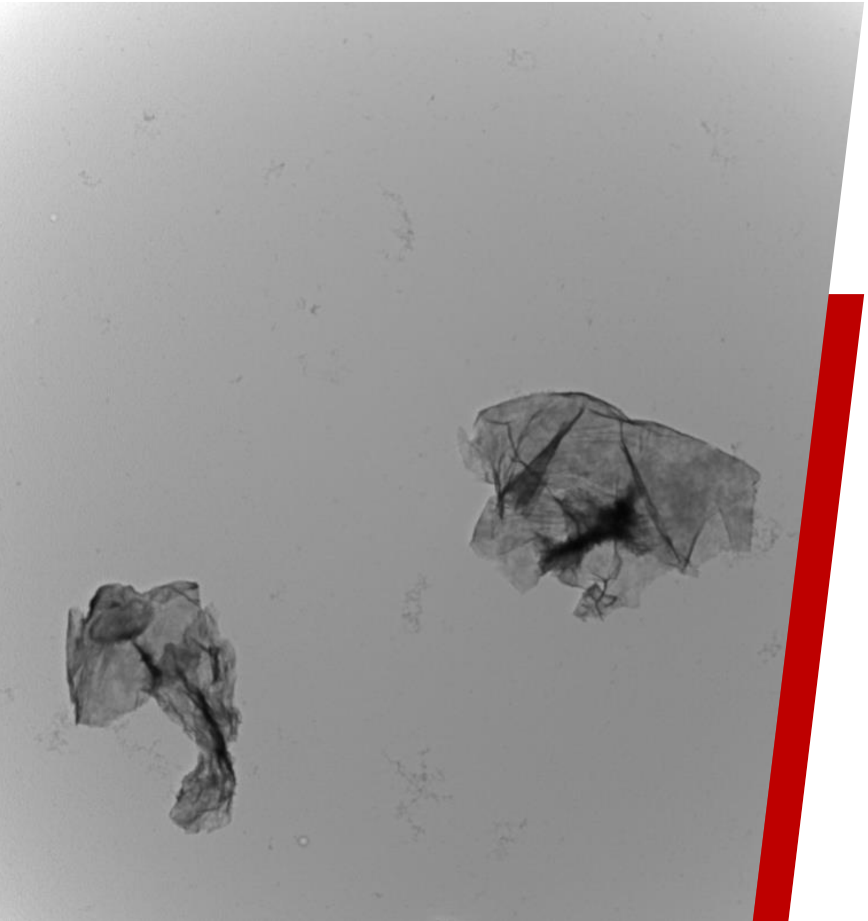


Empa
Materials Science and Technology

Challenges in the synthesis and characterization of 2D materials (Part 2)

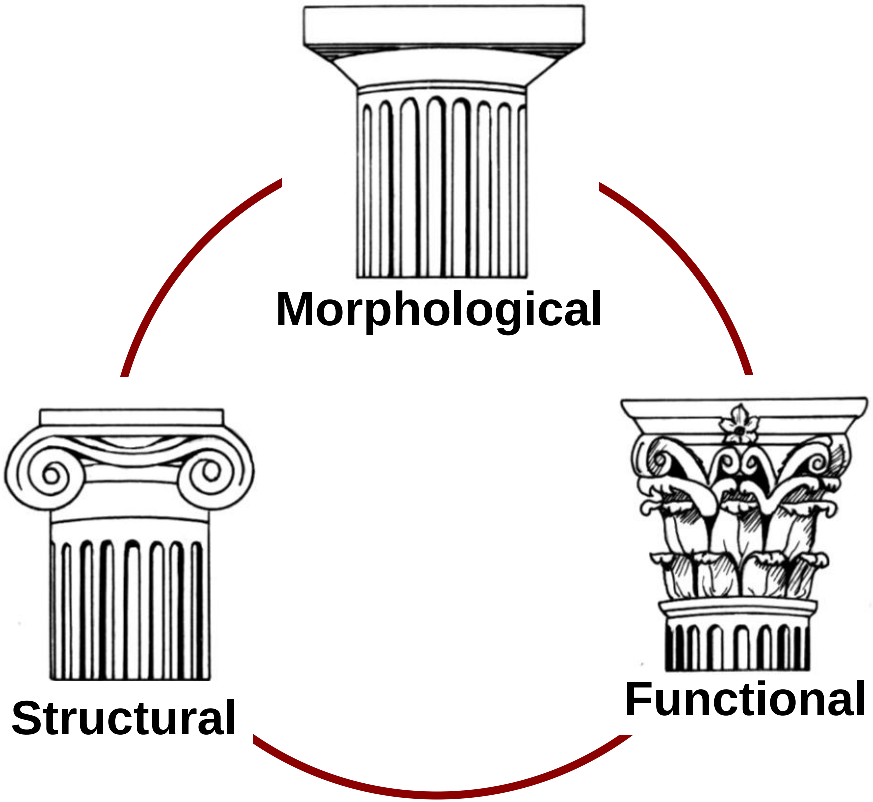
Dr. Giacomo Reina

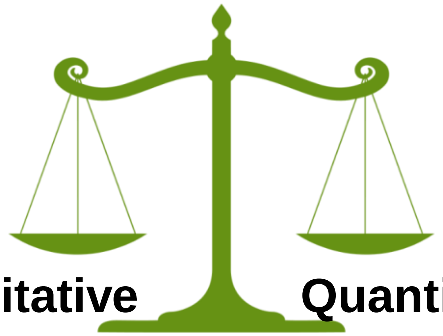
20.08.24 Visp

Outline

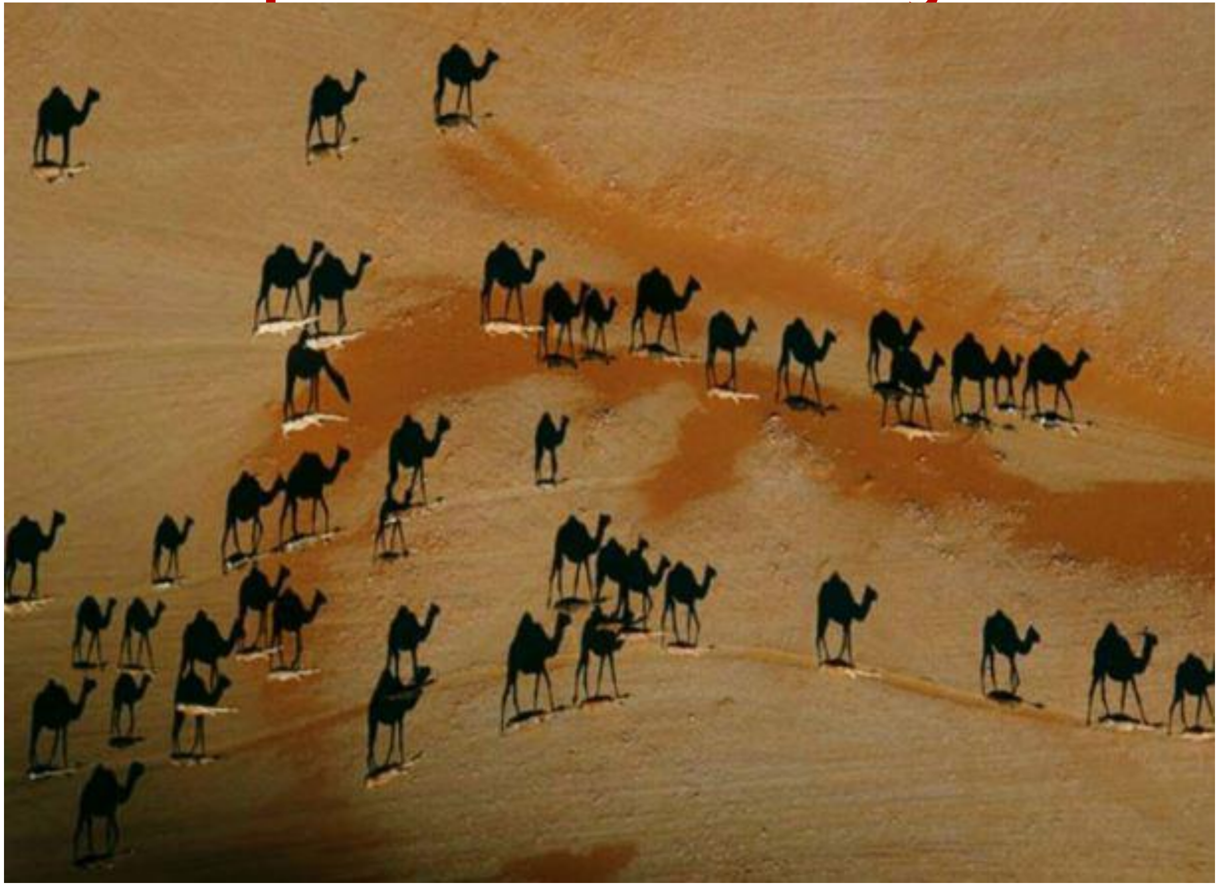
- 2D Nanomaterials: Timeline
- 2D Nanomaterials: Who are they?
- Synthetic Methods: Bottom-up
- Synthetic Methods: Top-Down
- Overview and Questions

The “pillars” of characterization





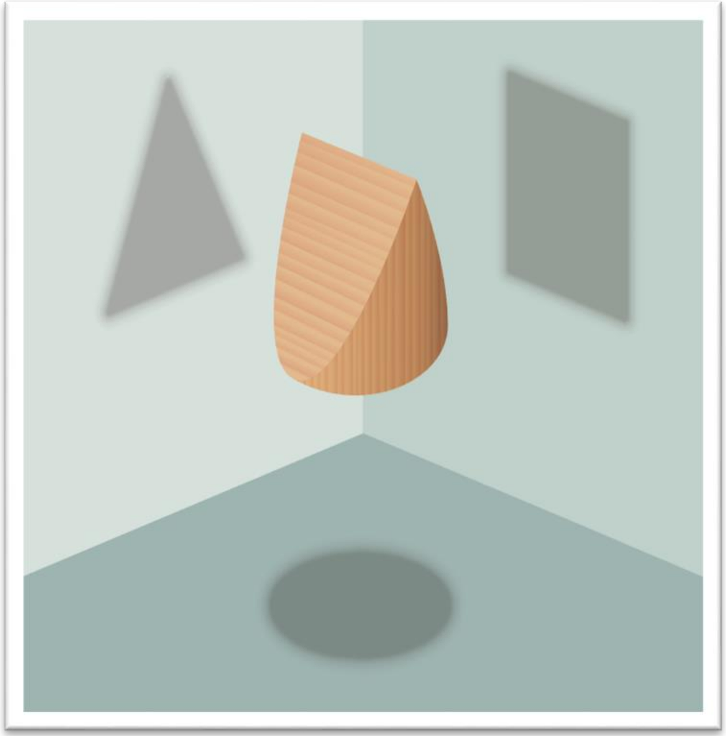
The viewpoint: bird-view vs frog-view



George Steinmetz, National Geographic 2005

Micro characterization vs Bulk

The combination of differentt methods is needed to understand the (nano)material completely



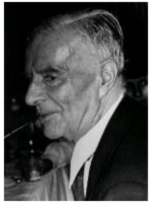
What can we measure to characterize NMs?

Interaction with EMF
(Spectroscopy)

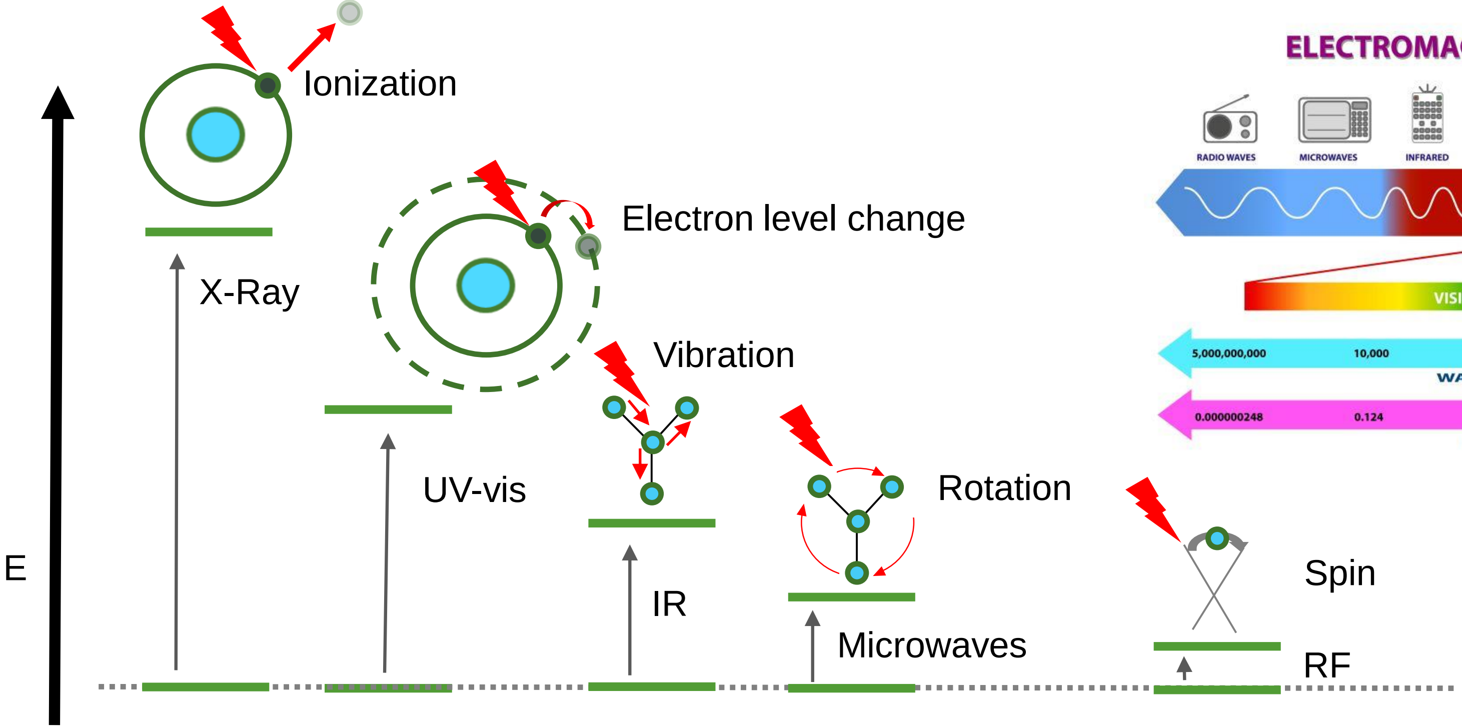
Mass changes
(Gravimetric)

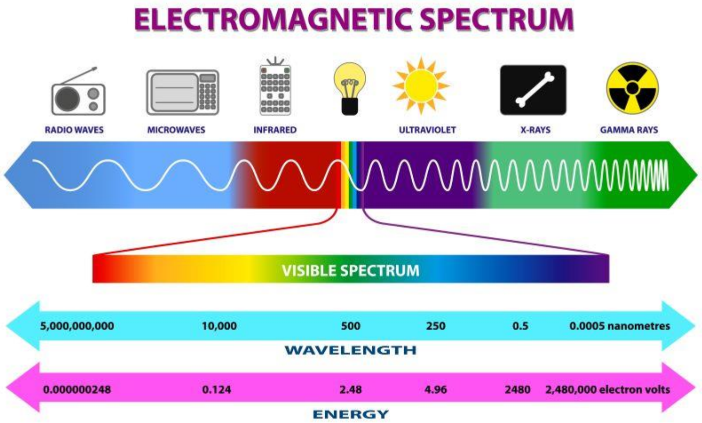
Physical interactions
(Scanning probes)

Interaction with electromagnetic field

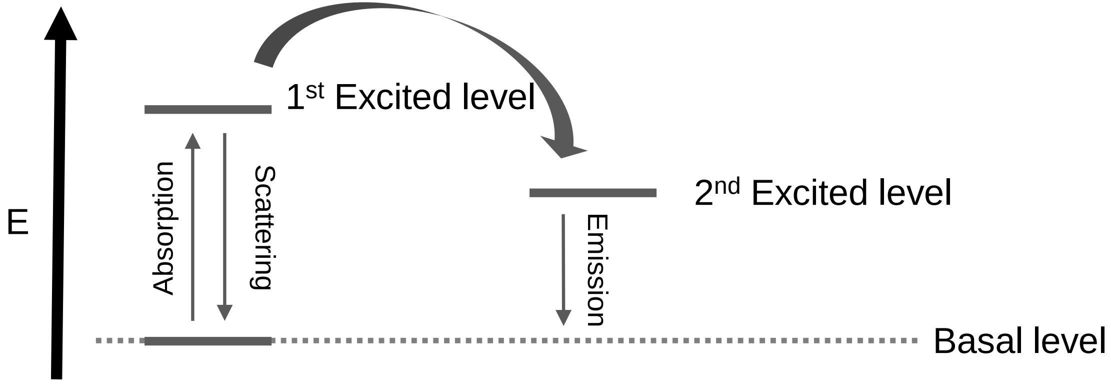


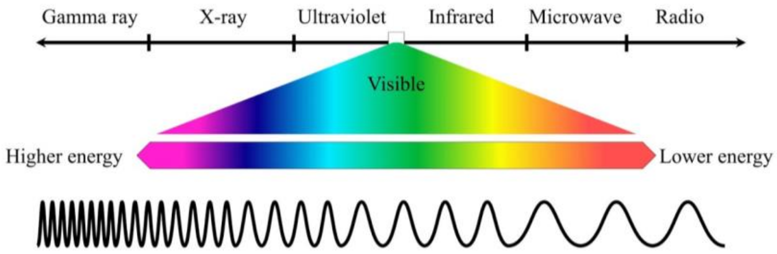
Aleksander Jabłoński



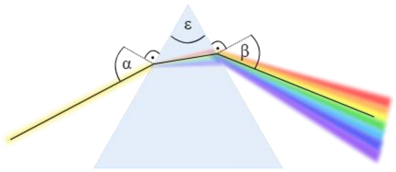


Interaction with electromagnetic field



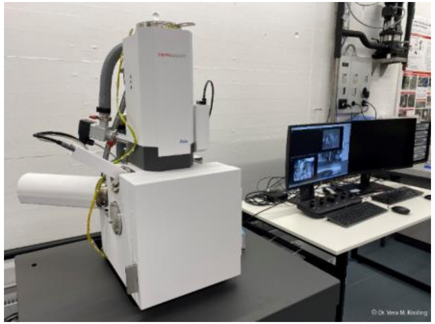


Absorbed energy > Emitted of energy

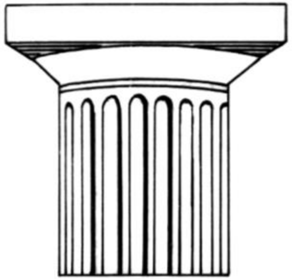


Diffraction

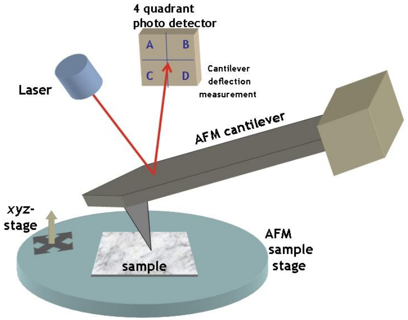
If we excite with green light where should we expect the emission?



SEM



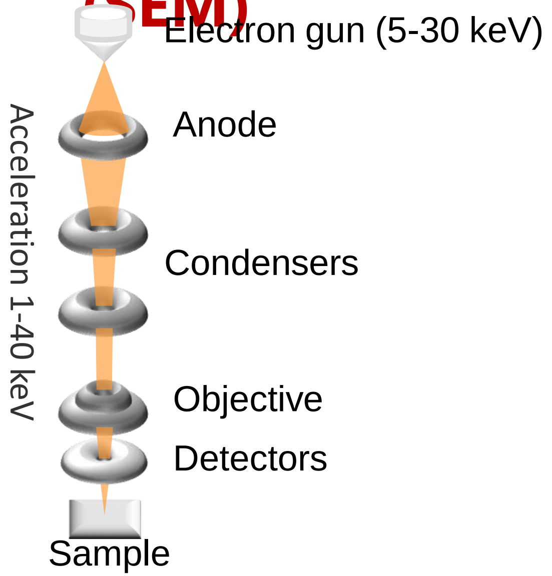
Morphological

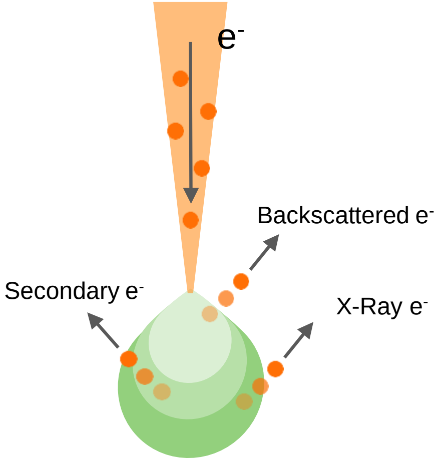


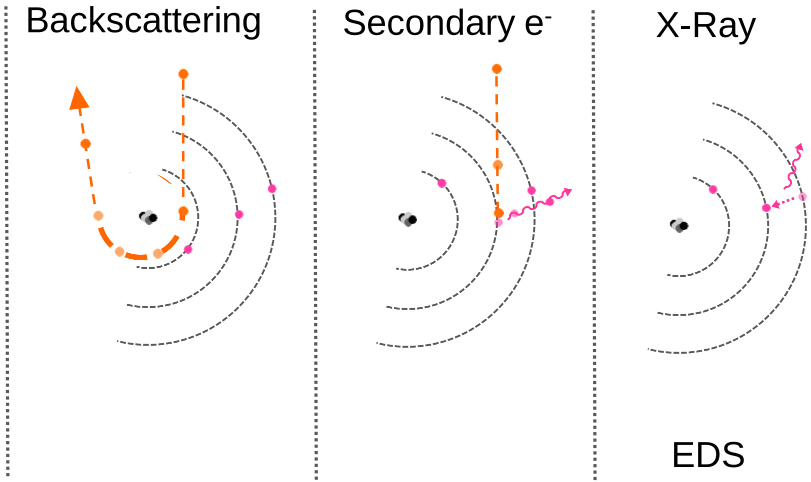
AFM

TEM

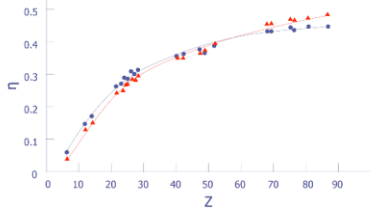
Morphology: Scanning Electron Microscopy (SEM)





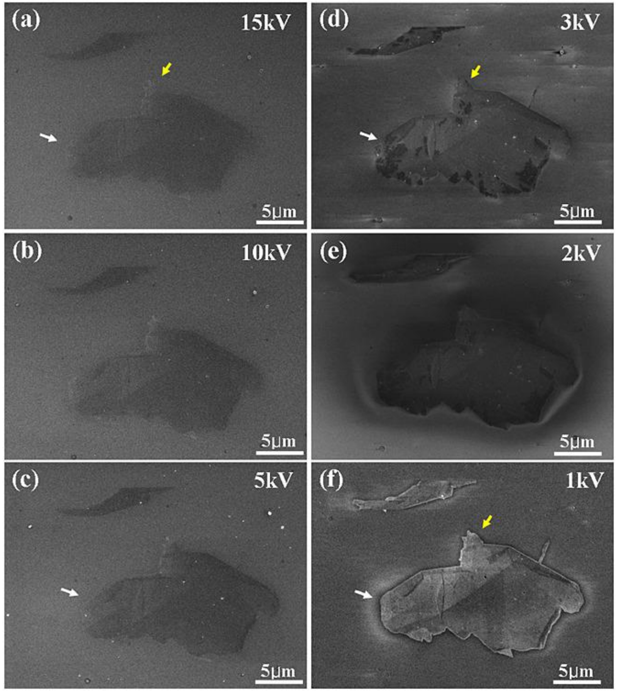


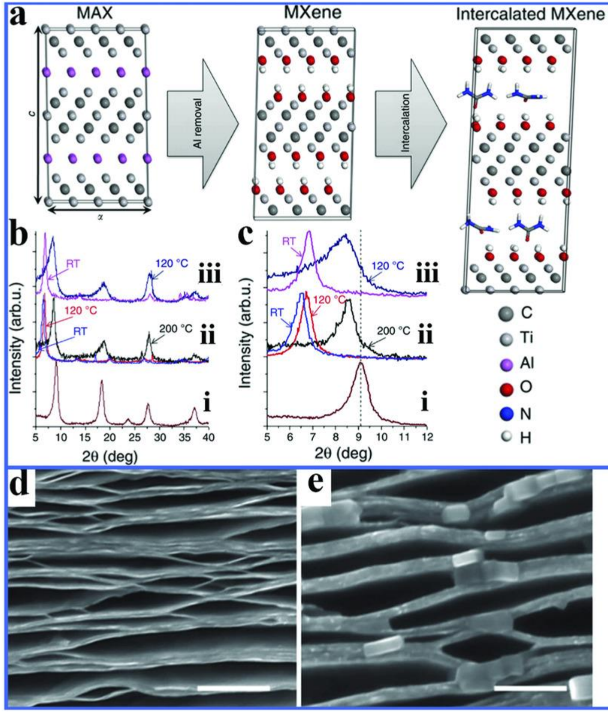
$$\eta = \frac{n_{BS}}{n_B}$$



Can you tell witch one is a scattering, absorption and emission process?

Morphology: Scanning Electron Microscopy (SEM)

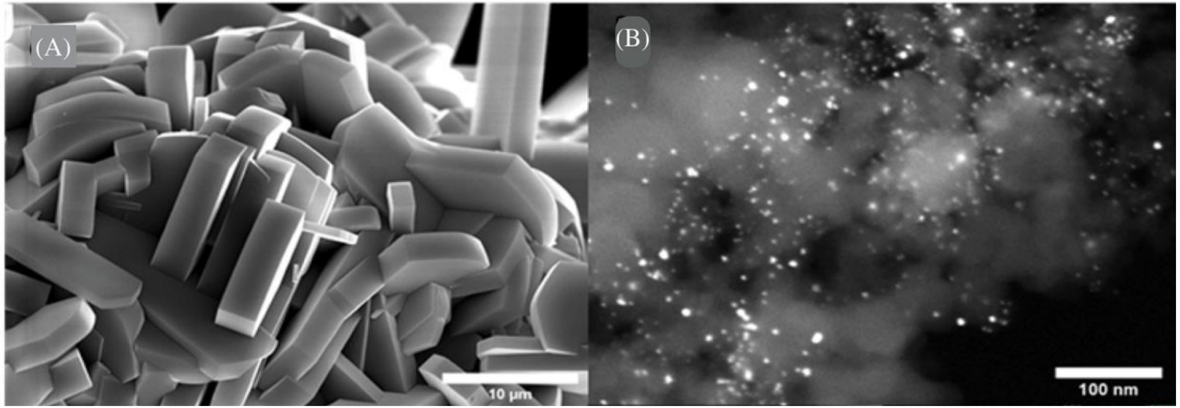




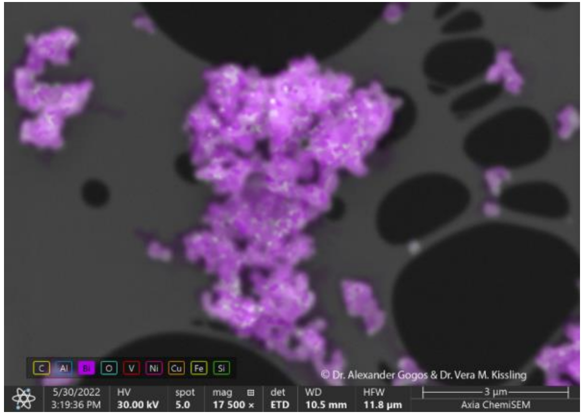
Yang et al. Surface and Interface Analysiss 2012
Wang et al. Advanced Energy Materials 2018

Morphology: Scanning Electron Microscopy (SEM)

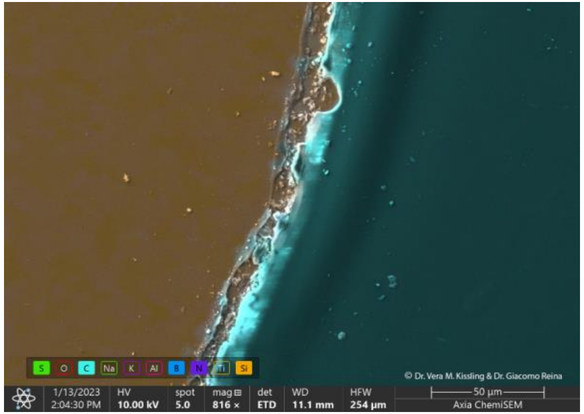
ETH zürich



(A) secondary electron image of silicon aluminium oxide using an in-lens secondary electrons (SE) detector; (B) backscattered electron (BSE) image of palladium nanoparticles, the particles appear as the brighter spots against the Al_2O_3 support.



Bismuth nanoparticle agglomerates



Nanoparticle-containing gel on glass

Davies, Thomas E., et al. *The Canadian Journal of Chemical Engineering* 2022

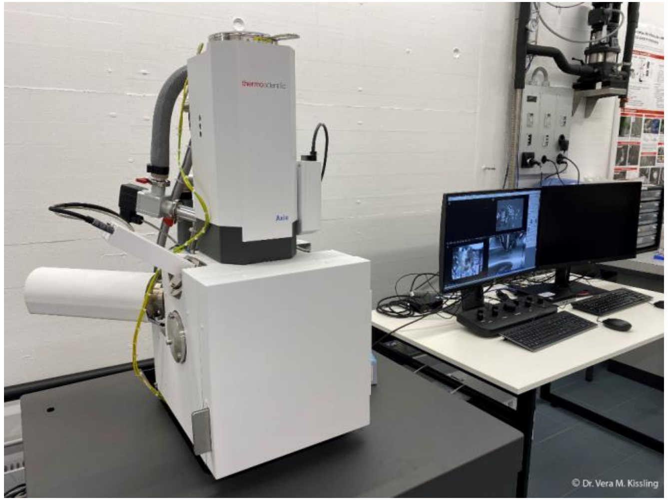
Morphology: Scanning Electron Microscopy (SEM)

Considerations:

- SEM is a common technique for NMs surface morphology characterization
- The sample is normally dried on a support (no limit about thickness or size)
- NMs made conductive
- Resolution is between 2 and 20 nm

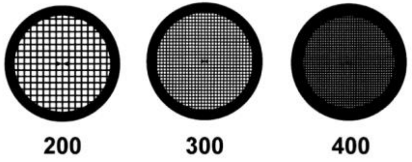
Applications:

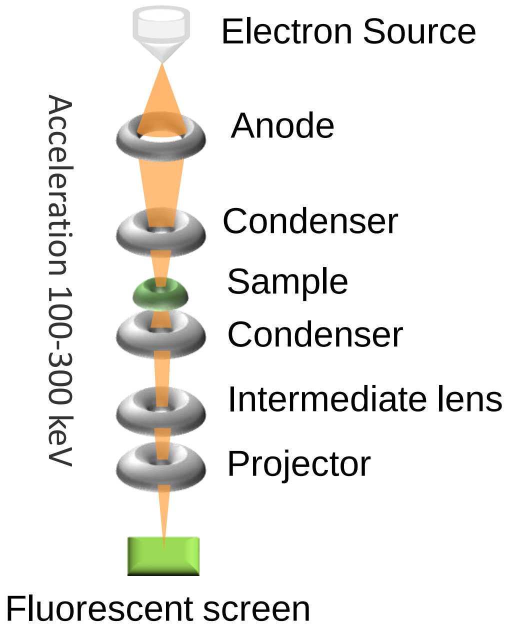
Surface analysis, surface morphology, microanalysis

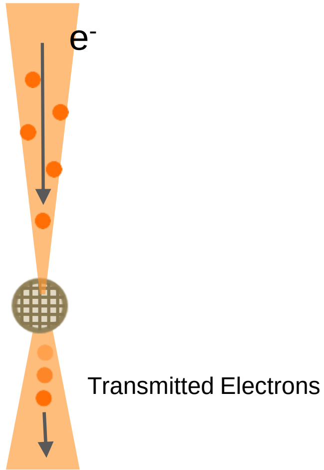


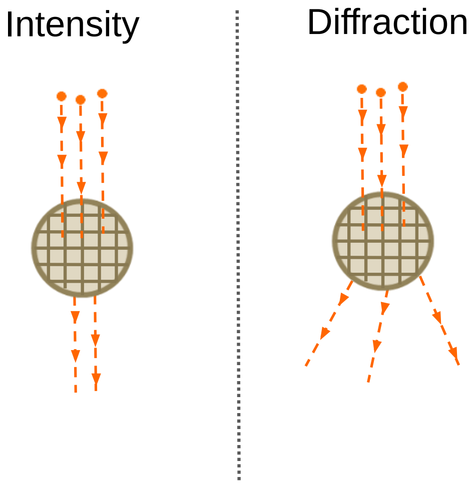
Do you know how to make NMs conductive?

Morphology: Transmission Electron Microscopy (TEM)





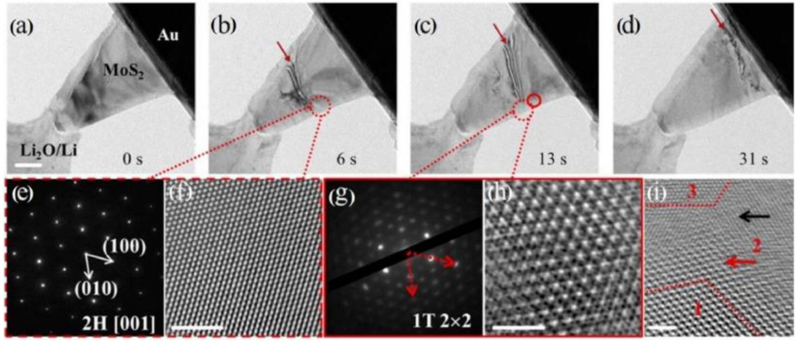


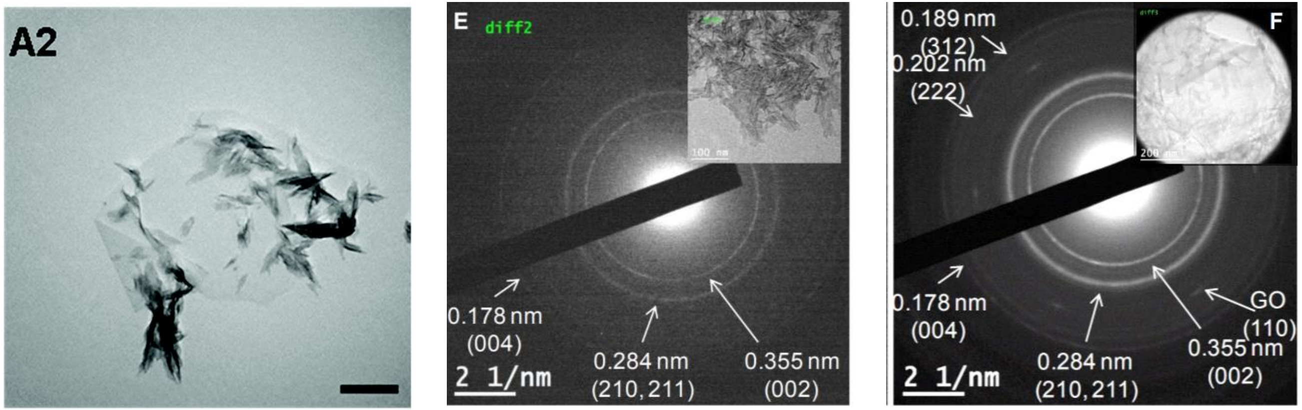


$$\lambda = 1.22 / E^{1/2}$$

TEM imaging a sample with 100 keV electrons is capable of a theoretical resolution of 0.004 nm.

Morphology: Transmission Electron Microscopy (TEM)





Reina et al. Nanoscale 2019, Szoszkiewcz et al. Surface Science Report 2022

Morphology: Transmission Electron Microscopy (TEM)

Considerations:

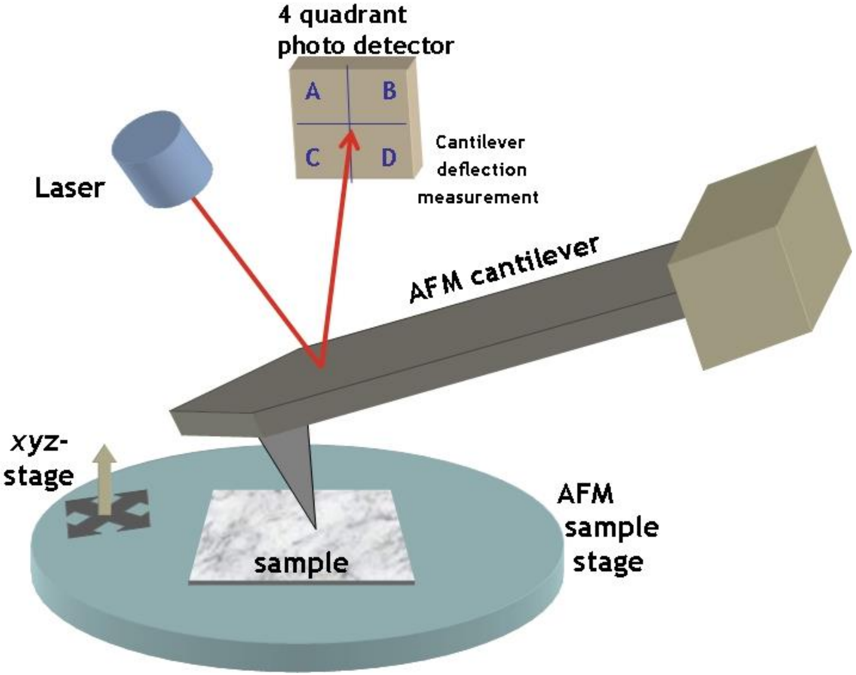
- TEM is a consolidated technique for NMs characterization
- The must be thin (<200 nm) and is deposited onto a special grid
- The instrument is expensive
- The sample preparation require “experts”
- Resolution is between 0.15 and 0.2 nm

Applications:

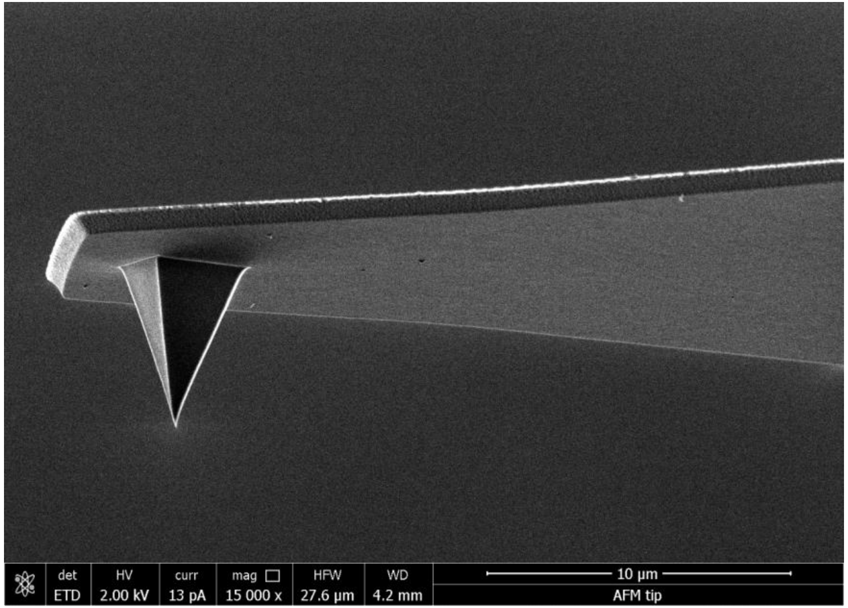
Surface morphology, microanalysis, size distribution

Morphology: Atomic Force Microscopy (AFM)

A very fine tip gropes the surface gradually. With the help of a LASER beam the movement becomes visible.

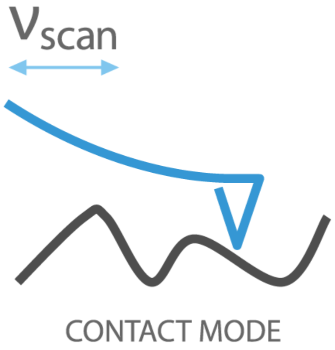


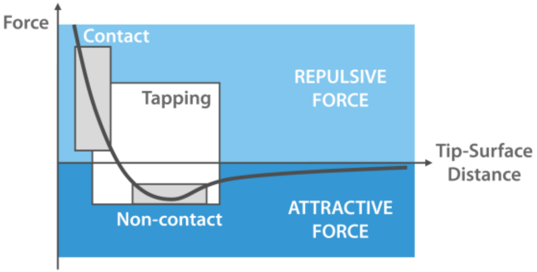
A cantilever scans the sample surface



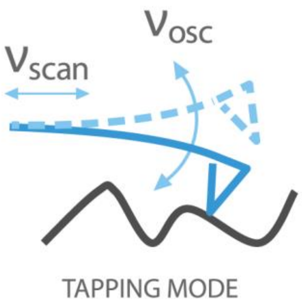
Morphology: Atomic Force Microscopy (AFM)

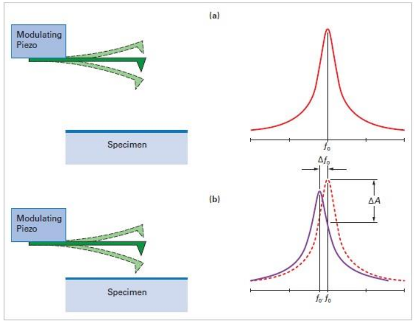
Contact Mode



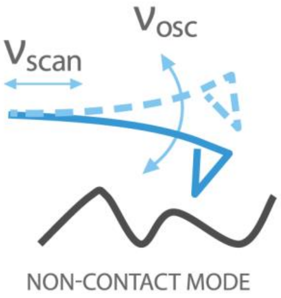


Tapping Mode

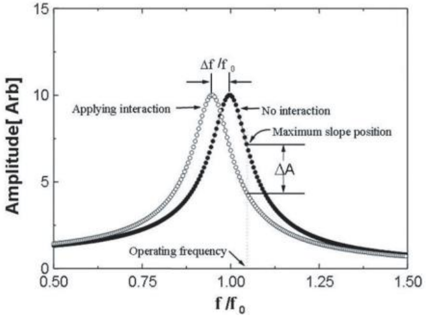




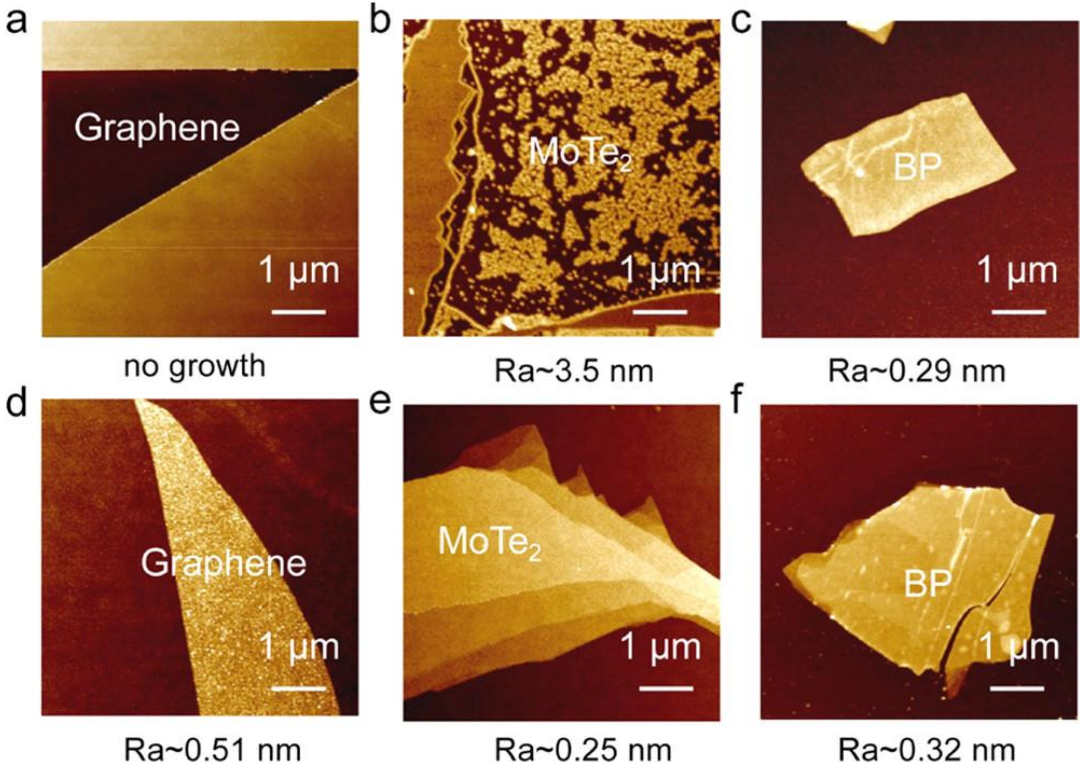
Non-Contact Mode

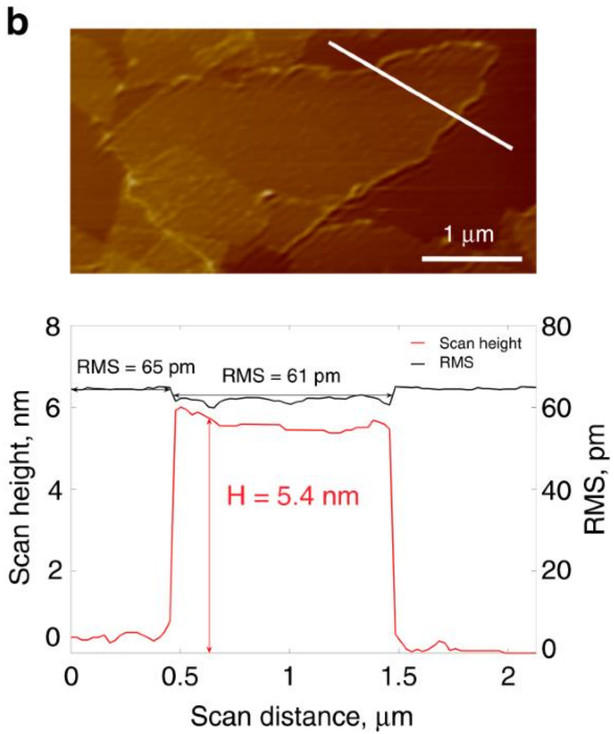


$$f_0 = \sqrt{\frac{k_0}{m}} \qquad f_{eff} = \sqrt{\frac{k_{eff}}{m}}$$



Morphology: Atomic Force Microscopy (AFM)





Mochalin et al. Nature Comm 2019, Chen et al. ACS App Mat Inter 2020

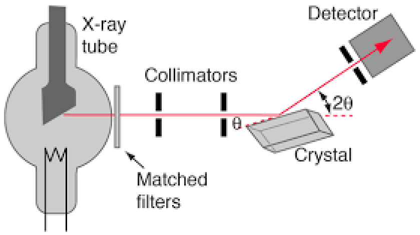
Morphology: Atomic Force Microscopy (AFM)

Considerations:

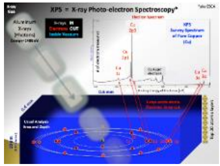
- AFM is physical technique to characterize the NMs morphology
- Depending of the NMs 3 techniques can be used
- AFM can be used at RT, atmospheric condition or in solution
- The analysis requires long time for acquisition
- Normally an “expert” is implied in the analysis

Mass spectrometry

Structural



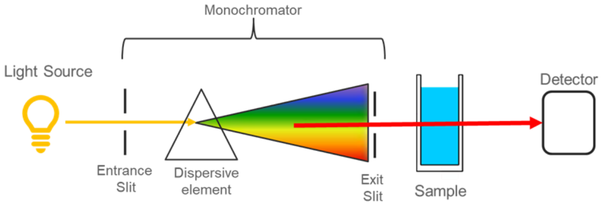
XRD



XPS

TGA

Raman



UV-vis spectrometry

Structural Characterizations: Thermogravimetric Analysis

The sample is weighed and placed in a pan.

The NMs are then placed in a controlled oven.

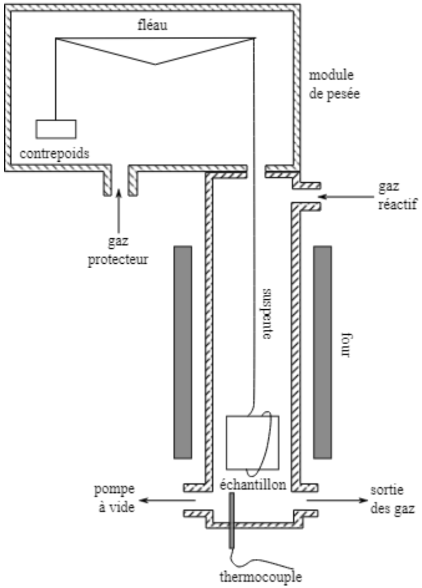
The oven is settled to a T ramp in a controlled inert or oxidizing atmosphere

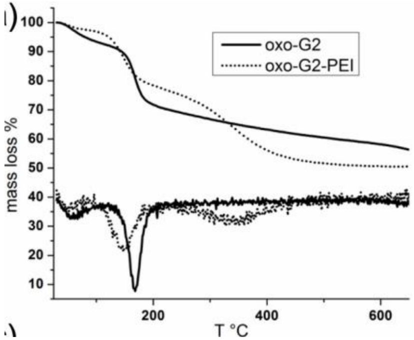
During the process, the weight of the sample is constantly measured

During the measurement the thermogram of the sample is measured

TGA is used also to quantify the functionalization.

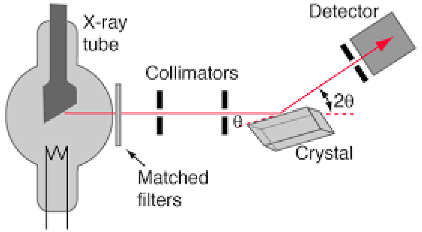
Differential analysis (DTG) is used to measure the T of decomposition





Reina et al. Carbon 2022

Structural Characterizations:
X-Ray Diffraction analysis (XRD)



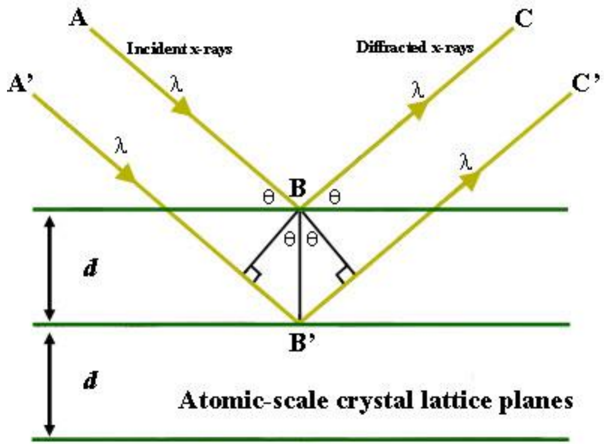
Atoms can scatter X-ray sources

A regular array of scatters produces a regular array of spherical waves

The scatter is constructive only in few specific directions according to the Bragg's law

$$2d\sin(\theta) = n\lambda$$

The average lattice structure size can also be determined by the Scheer law:

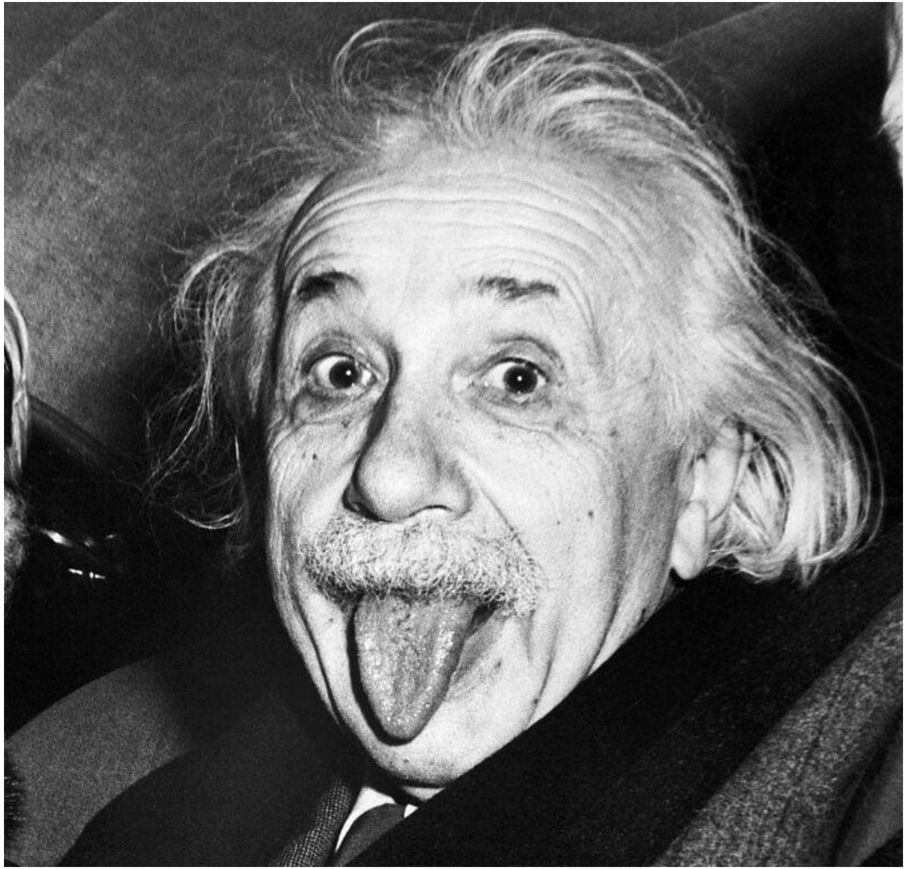


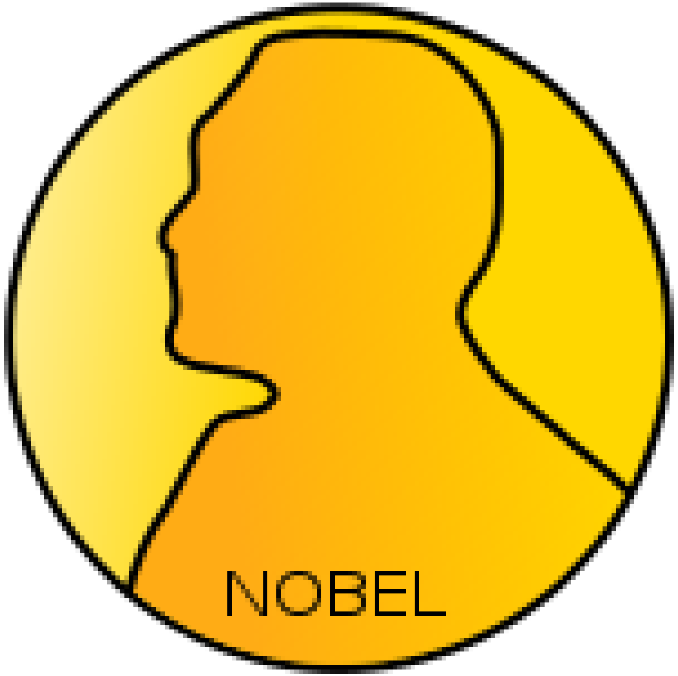
The spectra is then compared with literature or with a database

Used to analyze crystalline samples

Do you think that XRD is a bulk or a micro characterization?

Nobel Quiz





1921

Structural Characterizations:
X-Ray Photoelectron Spectrosco

XPS is based on photoelectric effect

The sample in a thin film is placed at high vacuum

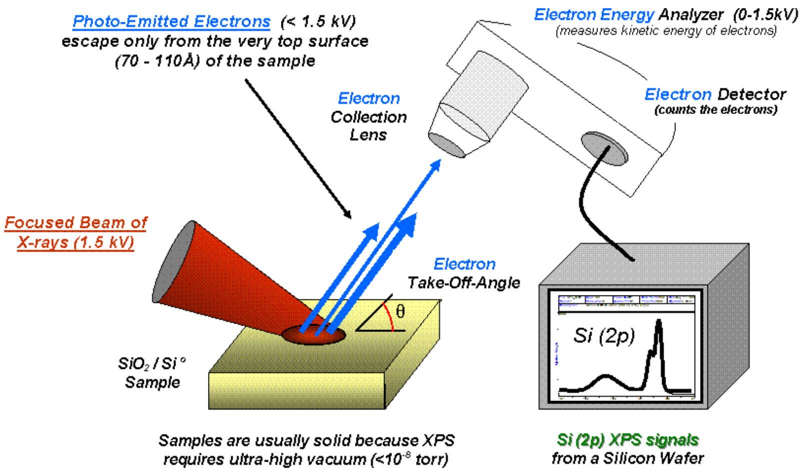
Monochromatic X-Ray source is used as excitation source

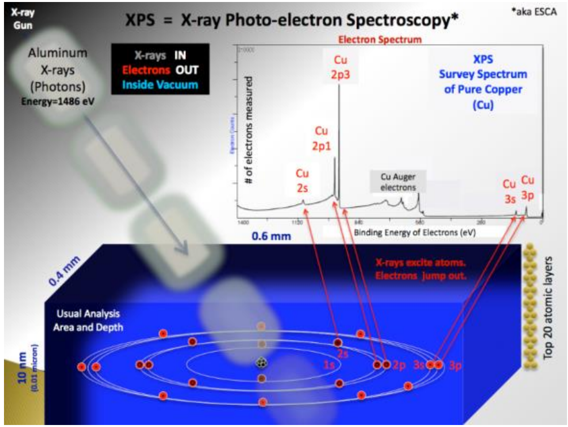
Electron are then collected and their binding energy is measured:

$$E_B = E_{photon} - (E_S + \varphi)$$

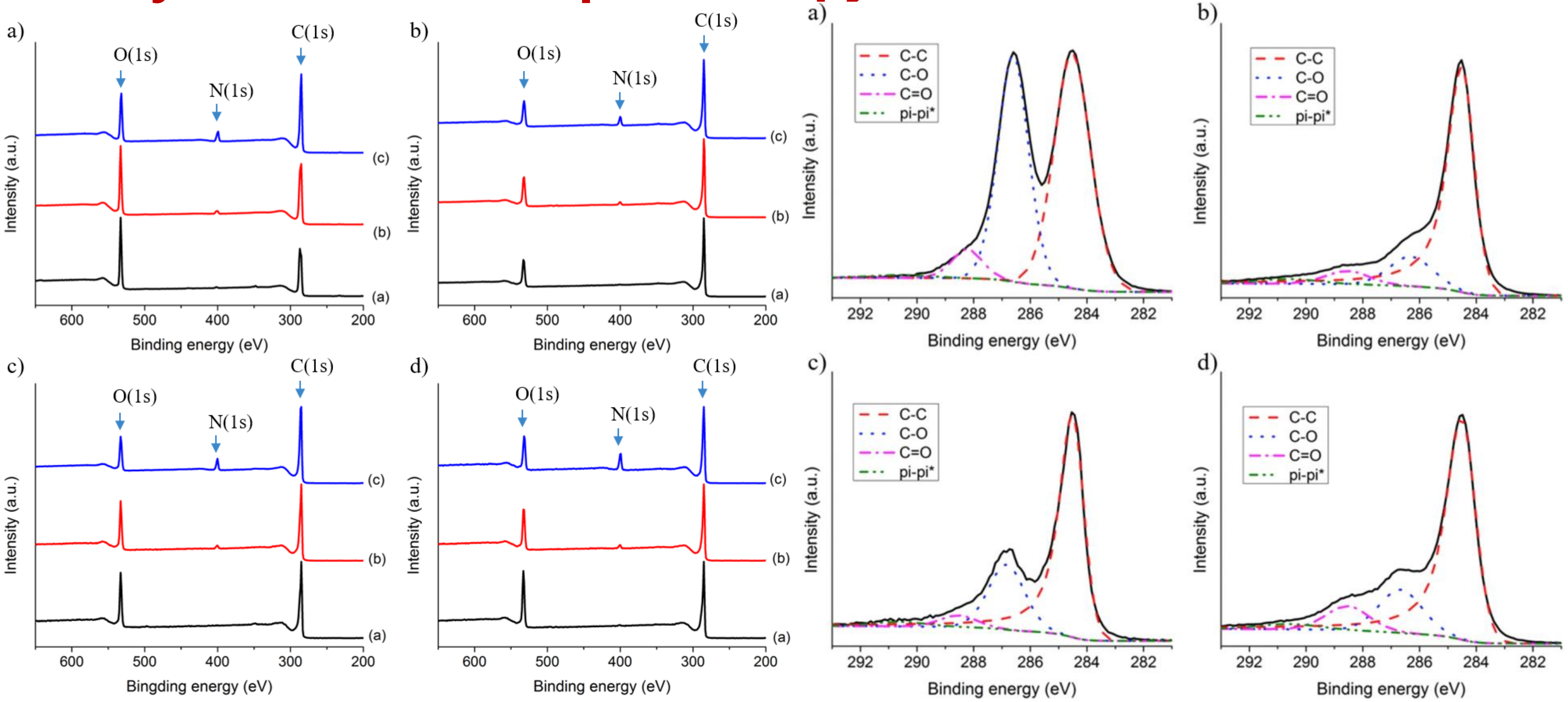
XPS is a surface technique (10 nm dept)

XPS is applied for any kind of NM



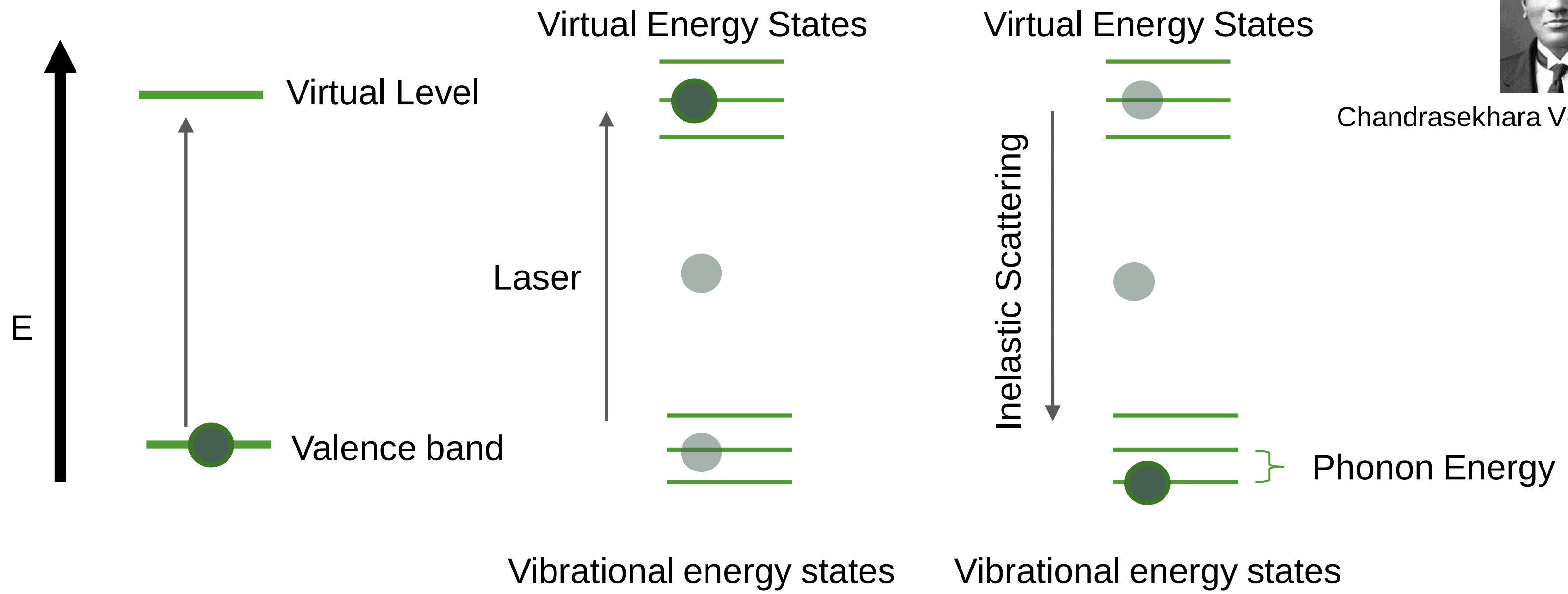


Structural Characterizations: X-ray Photoelectron Spectroscopy (XPS)



Chau et al. Carbon 2017

Structural Characterizations: Raman



Chandrasekhara Venkata Raman

$E_R = E_L - E_S$

Structural Characterizations: Raman

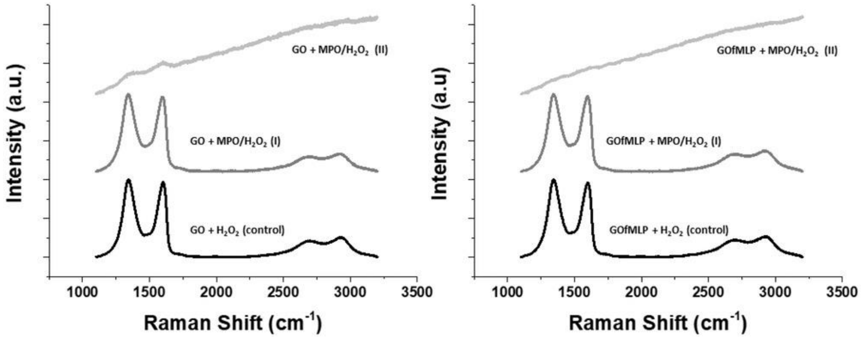
Raman Spectroscopy allows to precisely characterize the NMs

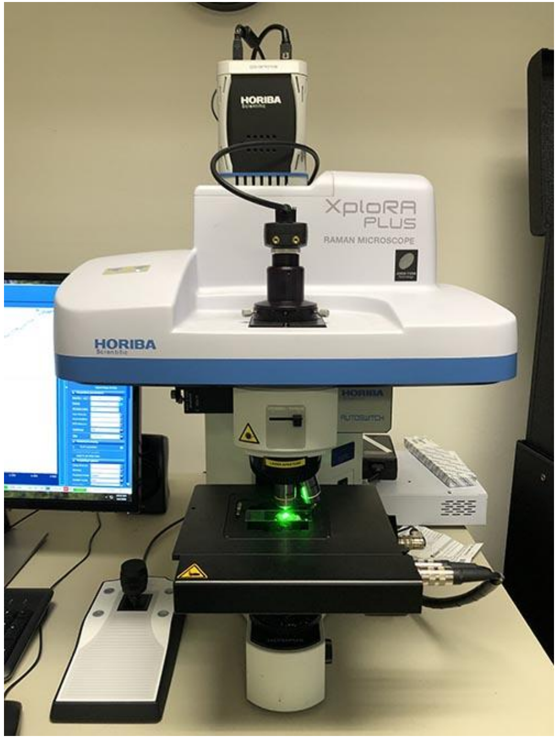
The NMs are normally in a film or placed on a solid substrate

The laser is coupled to a microscope that allows to select the area to analyze

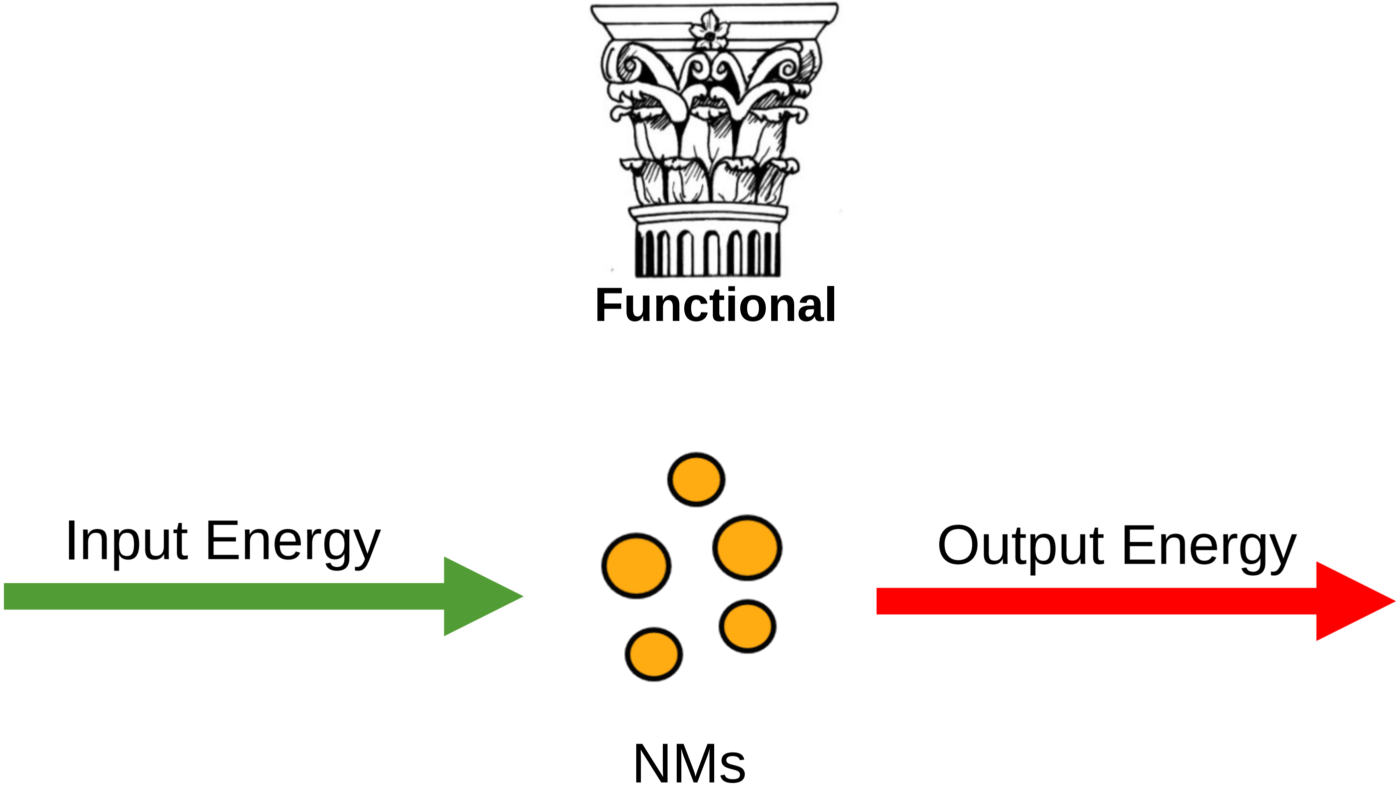
The Raman spectra is a unique fingerprint of the NM to analyze

Microanalysis of large area and mapping can be also performed

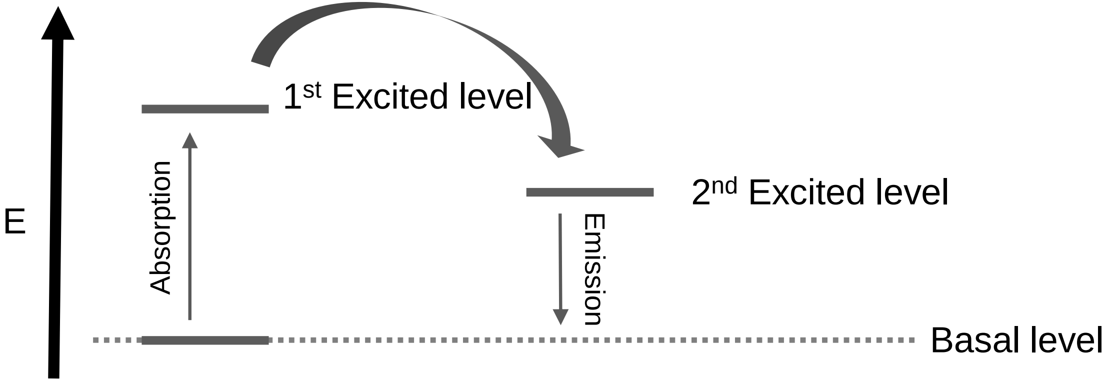


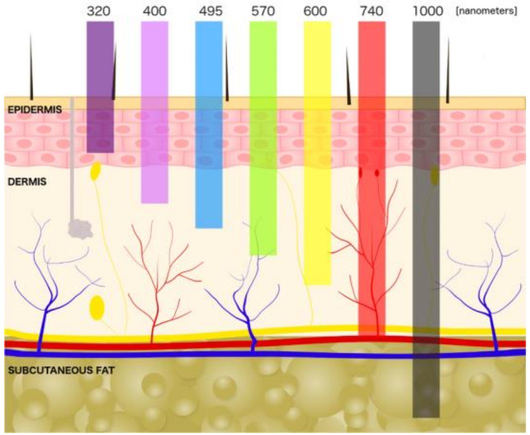


Martin et al. Advanced Functional Materials 2019

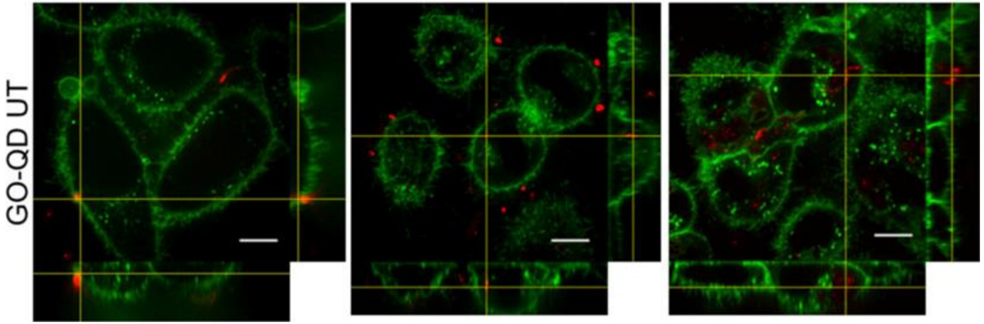

Functional
Input Energy
NMs
Output Energy

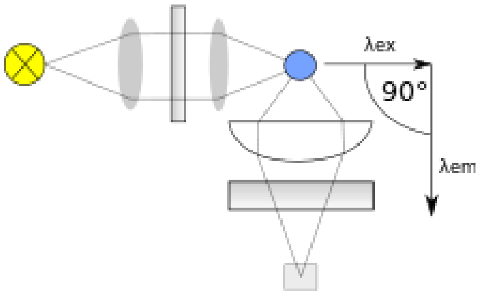
Functional Characterizations: Fluorescent bioimaging





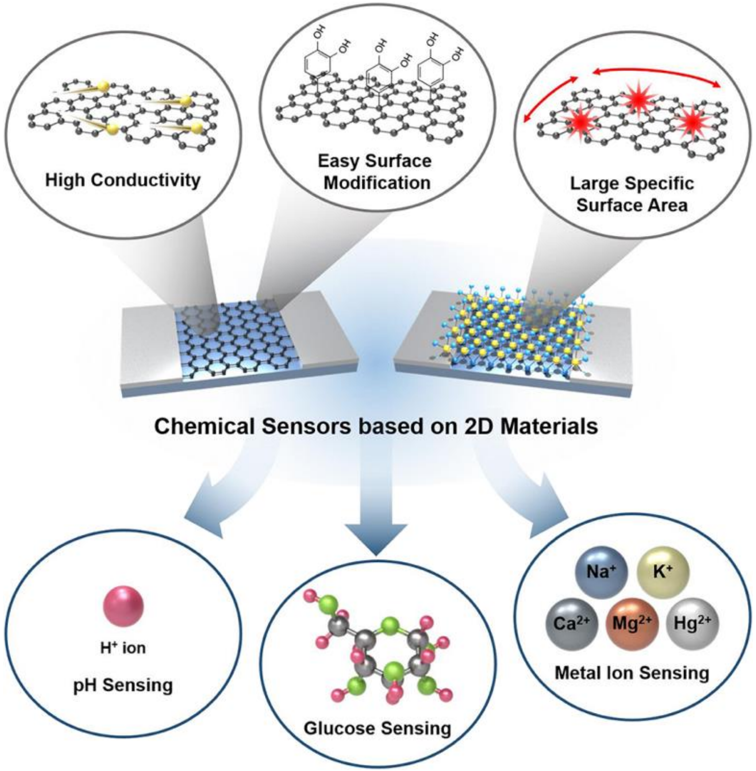
NMs are powerful imaging platform for their high stokes shits and quantum yield

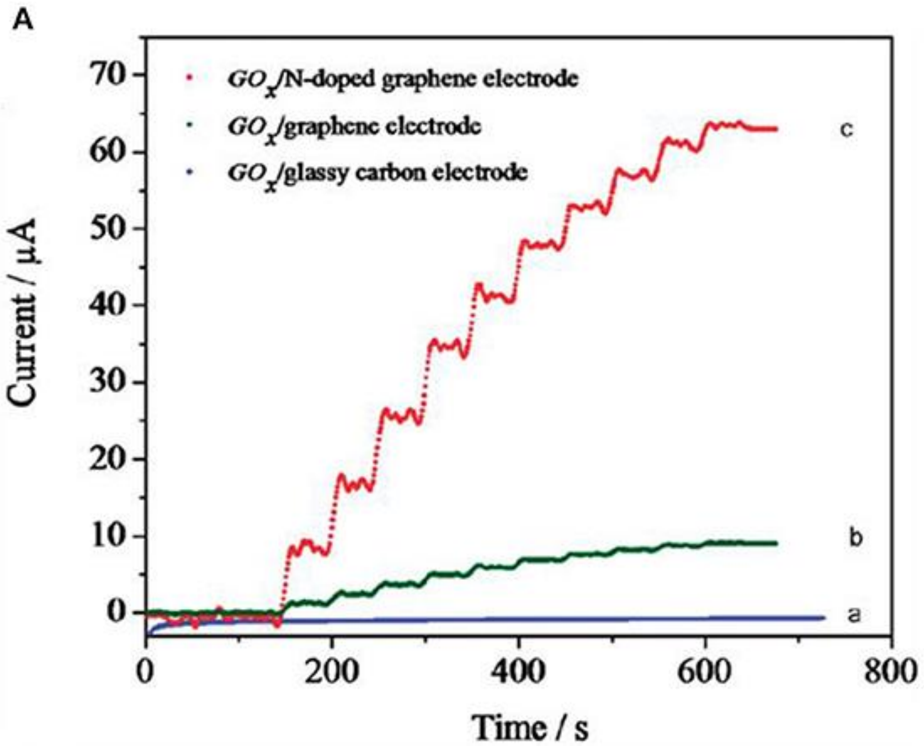




Reina et al. ACS Appliend Materias & Interfaces 2019

Sensing

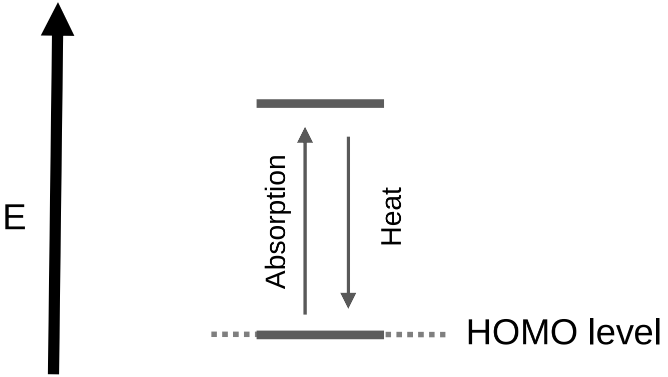


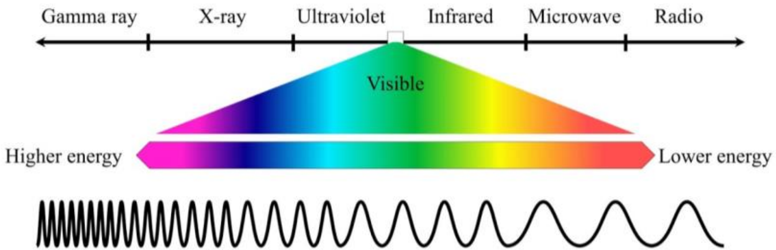


Jang et al. Front. Chem. 2019

Functional Characterizations: Photothermia

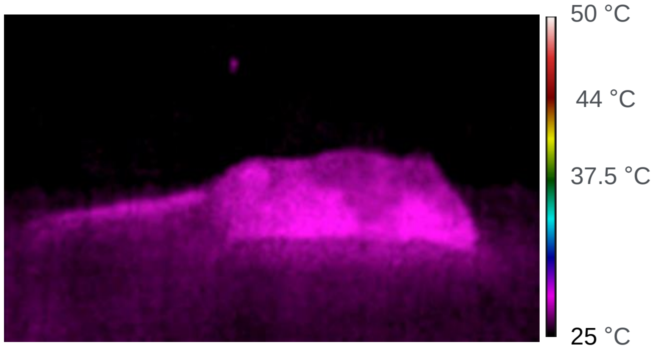
Functional Characterizations: Photothermia





Normally NIR light is used

$$\eta = \frac{hs(T_{Max} - T_{Surr}) - Q_{Dis}}{I(1 - 10^{-A_{980}})}$$



Conclusions

2D nanomaterials can be synthesized by different techniques.

We must first consider the final application of the 2D-NM.

Morphological, structural, and functional characterizations are imperative to assert the NMs.