

Caratterizzazione dei nano materiali

Amelia Montone

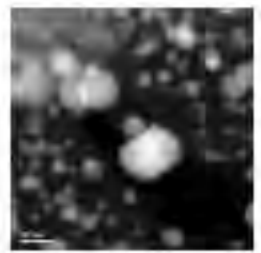
ENEA – Material Technology Unit, R. C. Casaccia, Roma (Italy)



Webinar ENEA
28 gennaio 2014

Classification of nanomaterials

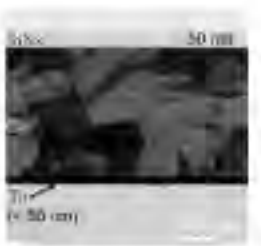
0-D
All dimensions (x,y,z) at nanoscale
 $d \leq 100 \text{ nm}$
Nanoparticles



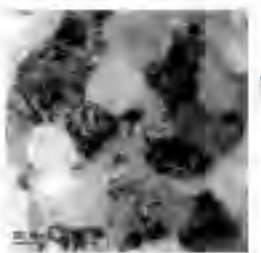
1-D
Two dimensions (x,y) at nanoscale, other dimension (L) is not
 $d \leq 100 \text{ nm}$
Nanowires, nanorods, and nanotubes



2-D
One dimension (t) at nanoscale, other two dimensions (L_x, L_y) are not
 $t \leq 100 \text{ nm}$
Nanocoatings and nanofilms



3-D
No bulk dimension at nanoscale
Nanocrystalline and nanocomposite materials

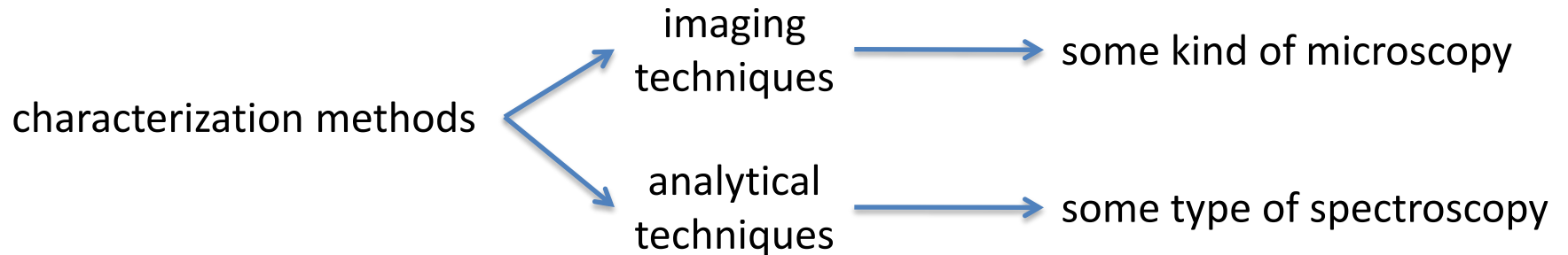
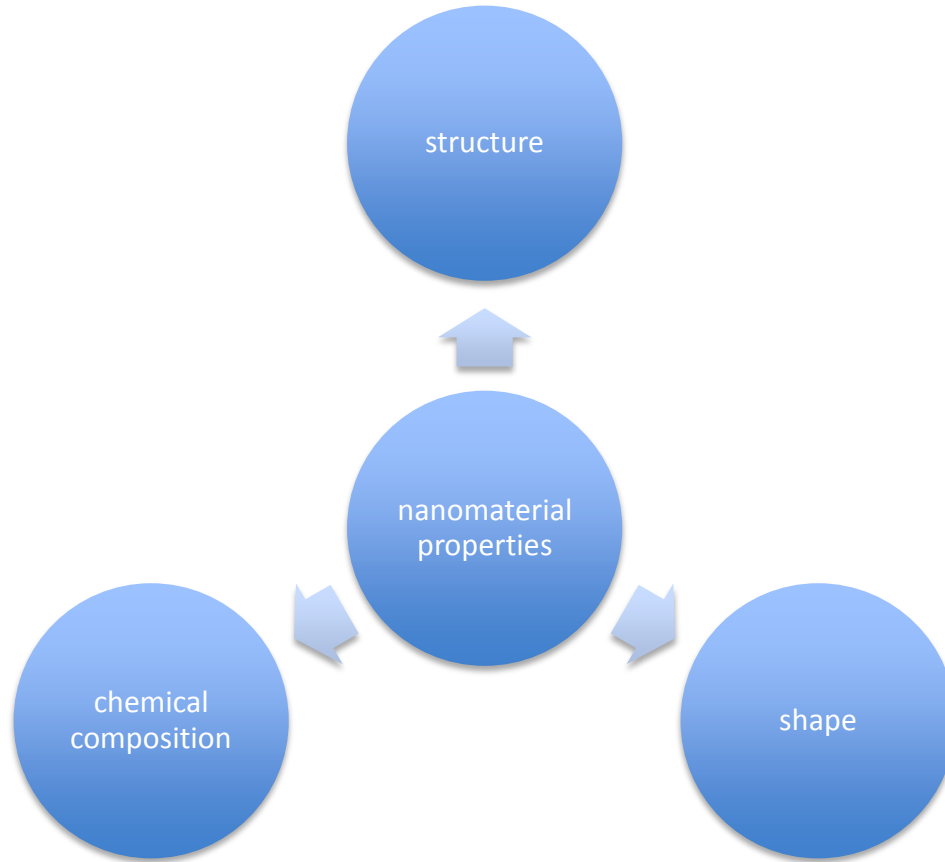


3 dimensions at nanoscale
1 dimensions outside the nanoscale
ad so on...

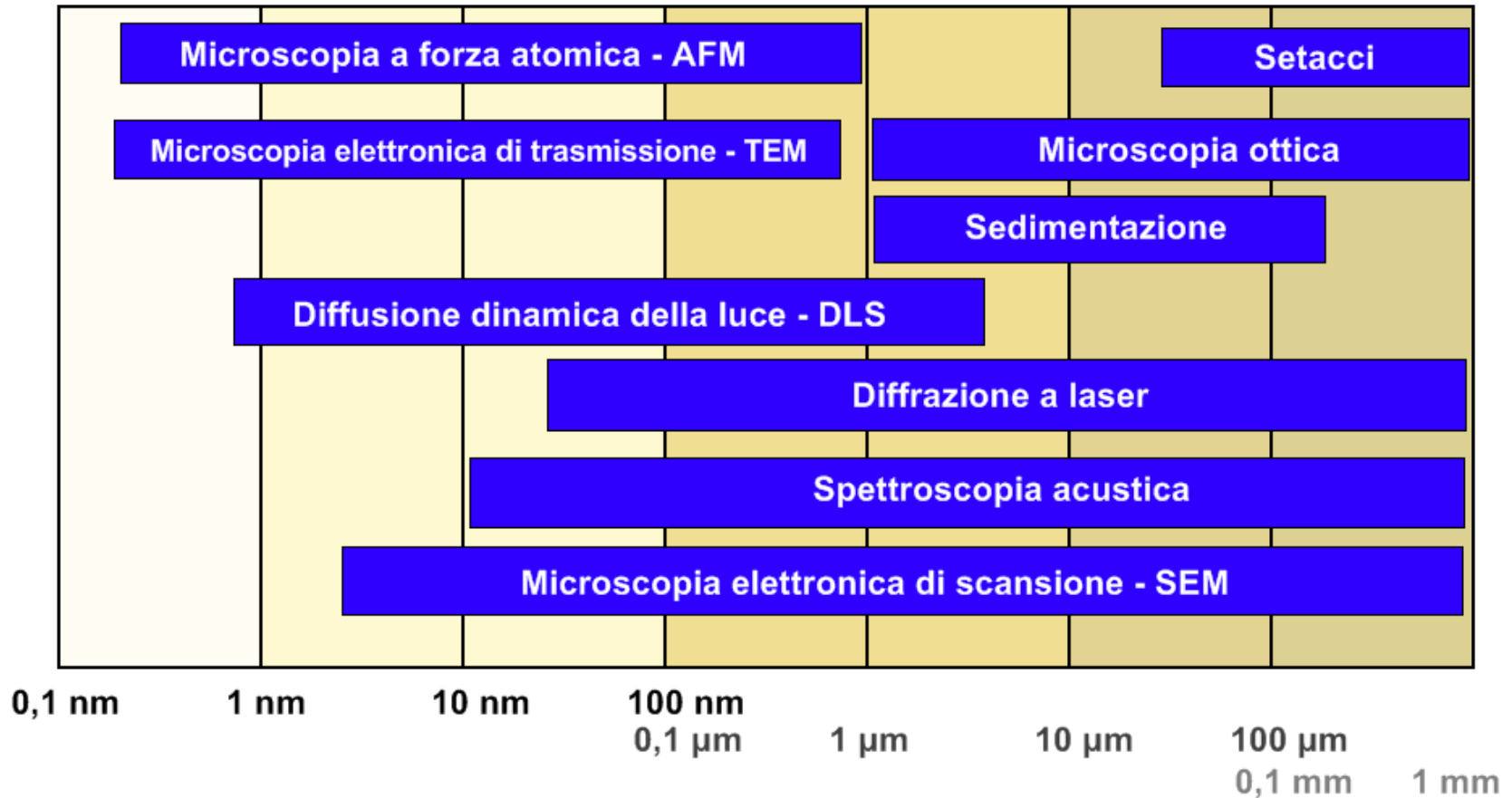
nanomaterials can be...

- amorphous or crystalline
- single crystalline or polycrystalline
- composed by single or multichemical elements
- Exhibit various shapes and forms
- Exist individually or incorporated in a matrix
- metallic, ceramic, or polymeric

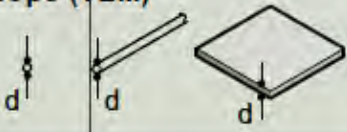


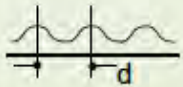
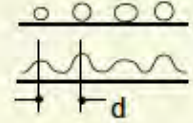
The role of the characterization



Types of characterization techniques



Types of characterization techniques

	Near Field and Confocal Light Microscopy Size Shape Topography 3D image reconstruction (confocal)	
Transmission Electron Microscope (TEM) Size Composition Crystal structure (inferred)		
	Scanning Electron Microscope (SEM) Size and shape Microstructure Composition Topography Grain orientation	
Xray Size Crystal Strain		
Atomic Force Microscopy (AFM) Topography/surface profile Surface mapping Mechanical properties		
Spectroscopy Chemical composition Chemical bonding		

Optical /Confocal Microscopy

Diffraction limit defines spatial resolution, fraction of μm range

First place you want to 'look'



“Non Conventional” Optical /Confocal microscopy

**Near-Field Scanning Optical Microscope
(NSOM)**

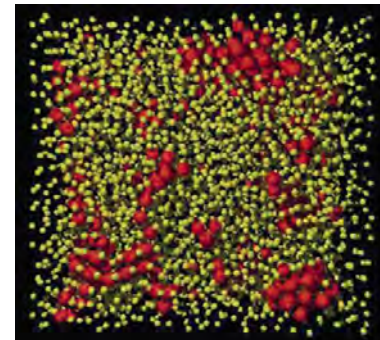
resolution 50 nm

Confocal Scanning Light Microscope

lateral resolution 100– 200 nm,

vertical resolution 400– 500 nm.

3-D image of the specimen



Electron Microscopy

Diffraction limit defines spatial resolution, fraction of nm range

Why electrons?

Spatial resolution of whichever instrument using lenses for obtaining a magnified image of an object is limited by diffraction effects to a minimum value essentially determined by the wavelength.

$$R = 0,61\lambda/n \sin\alpha \quad (\text{E. Abbe 1873})$$

Visible light has wavelength in the fraction of mm range, while interatomic distances are about three order of magnitude smaller.

Electron wavelength depends on the kinetic energy according to the De Broglie equation.

$$\lambda = 1.22/E^{1/2} \quad (\text{De Broglie 1926})$$

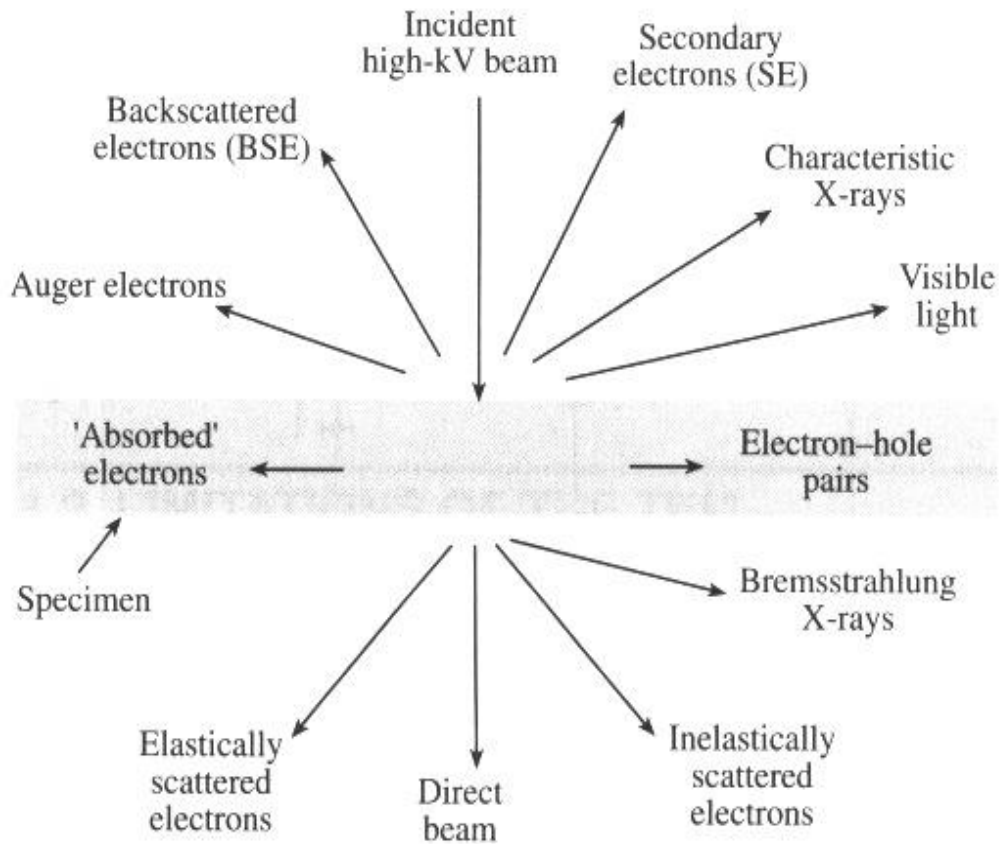
Table 1.2. Electron Properties as a Function of Accelerating Voltage

Accelerating voltage (kV)	Nonrelativistic wavelength (nm)	Relativistic wavelength (nm)	Mass ($\times m_0$)	Velocity ($\times 10^8$ m/s)
100	0.00386	0.00370	1.196	1.644
120	0.00352	0.00335	1.235	1.759
200	0.00273	0.00251	1.391	2.086
300	0.00223	0.00197	1.587	2.330
400	0.00193	0.00164	1.783	2.484
1000	0.00122	0.00087	2.957	2.823

Electron Microscopy

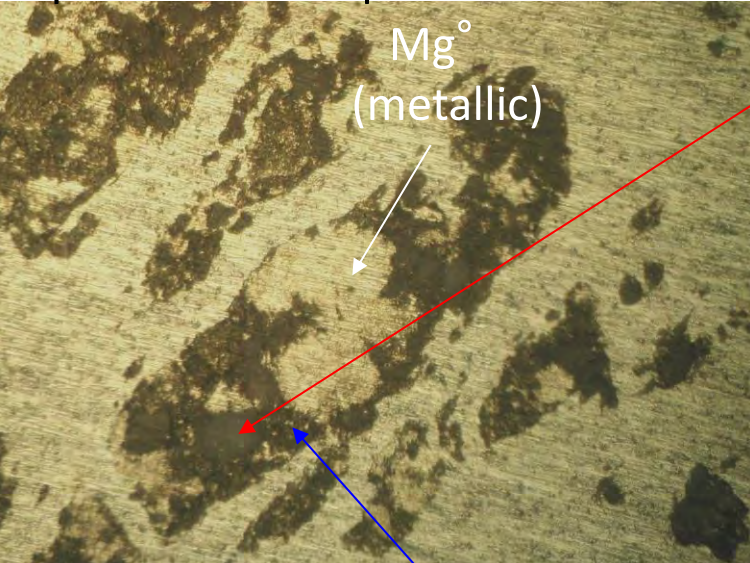
*Scanning Electron Microscopy (SEM),
Transmission Electron Microscopy (TEM),
Scanning Transmission Electron Microscopy (STEM).*

every signal
gives a different
kind of
information

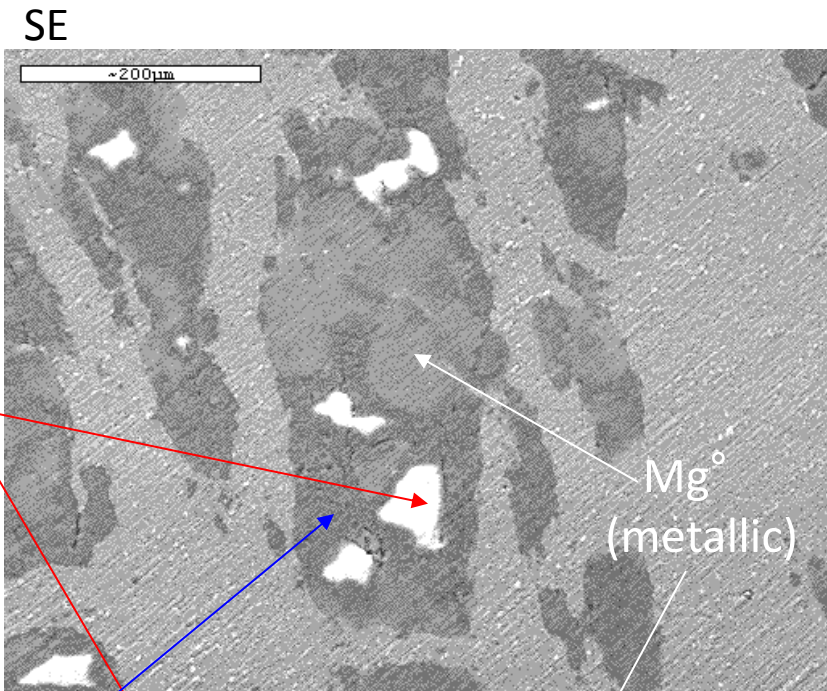


Some examples (SEM)

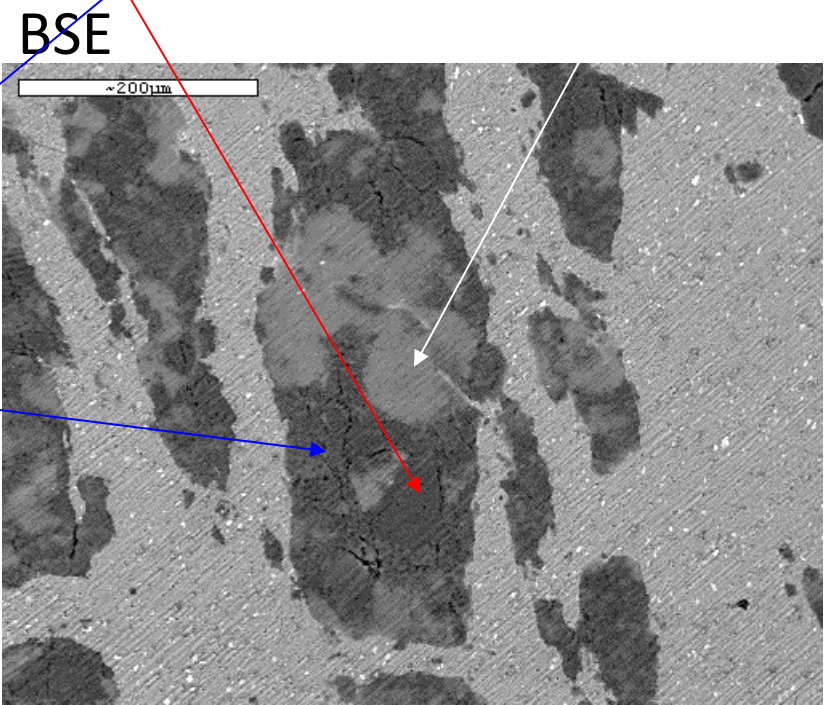
Optical Microscope



Phase A



Phase B

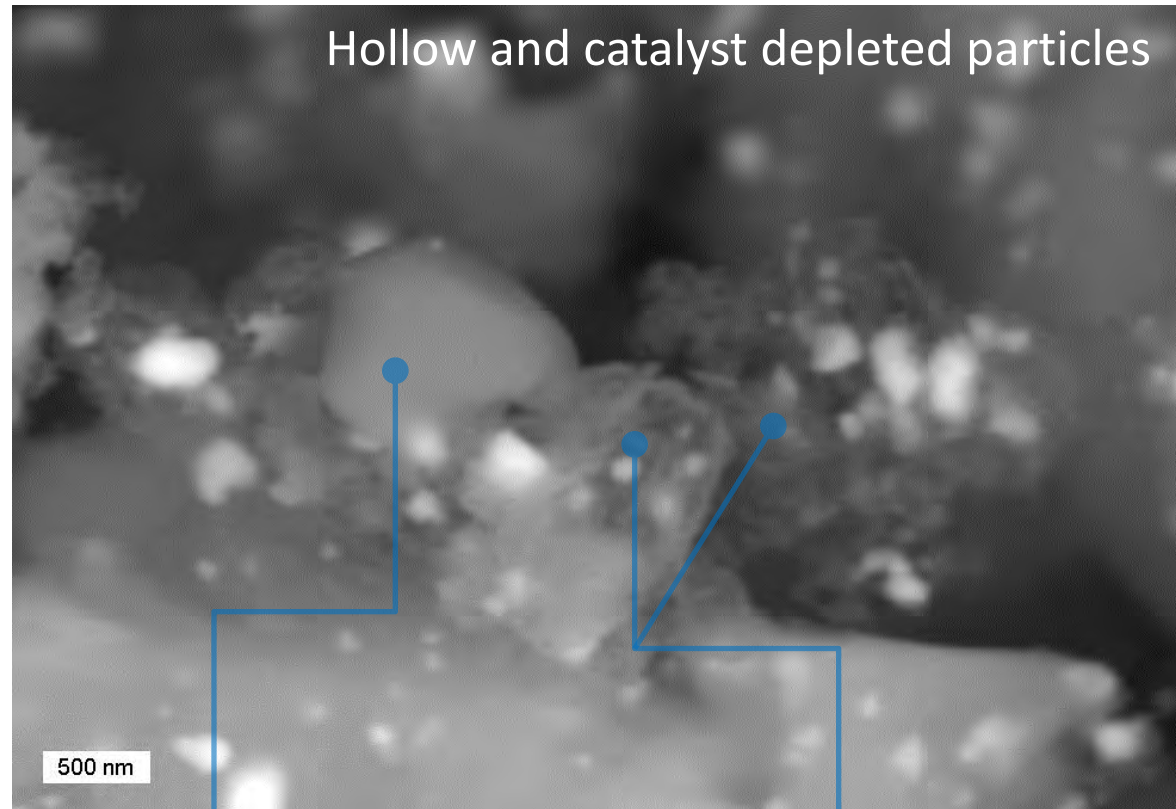


Mg/MgH₂ 10h milled
conductive matrix (aluminium)

Some examples (SEM)

SEM: powder of the pellet

$\text{MgH}_2 + 10\text{Nb}_2\text{O}_5 + 5\text{ENG}$ – after cycling

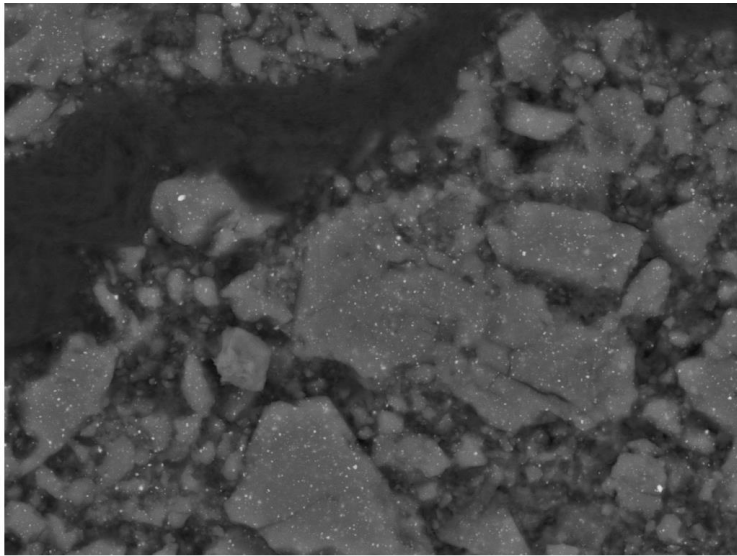


Catalyst depleted
particles

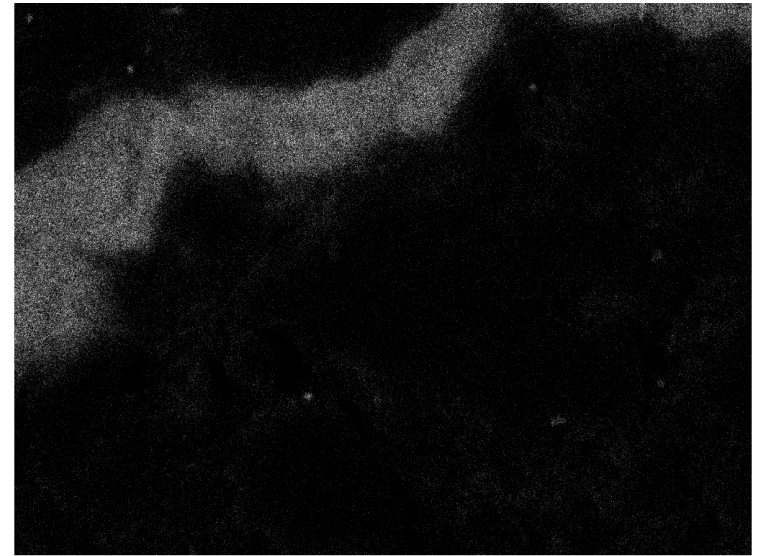
Hollow particles

Some examples (SEM)

~600MPa – Nb₂O₅



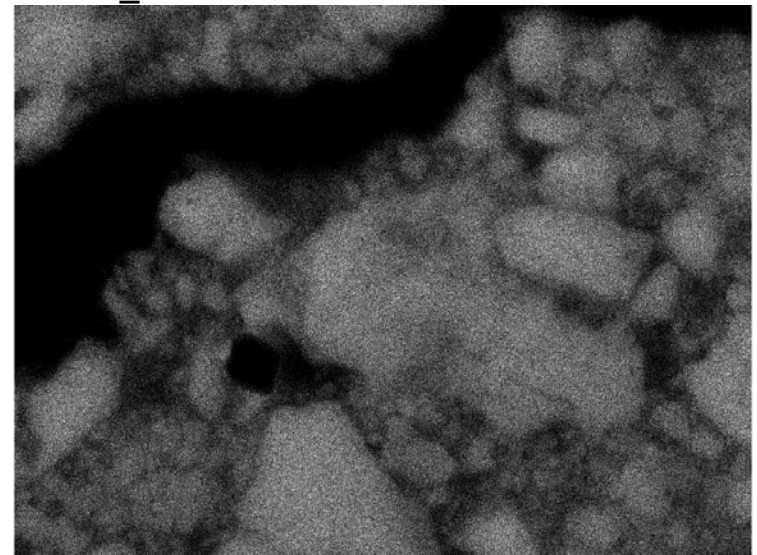
Electron Image 1



C Ka1_2

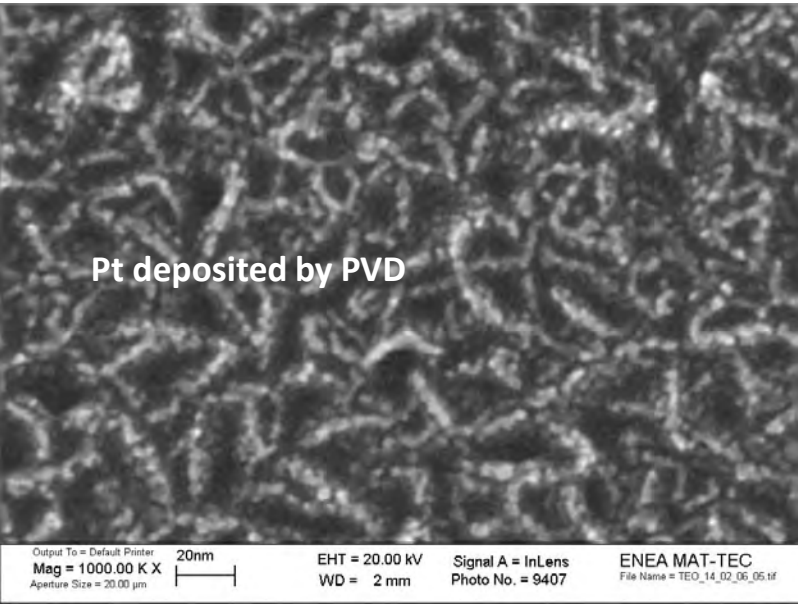
MgH₂ + 5wt% ENG

EDS map

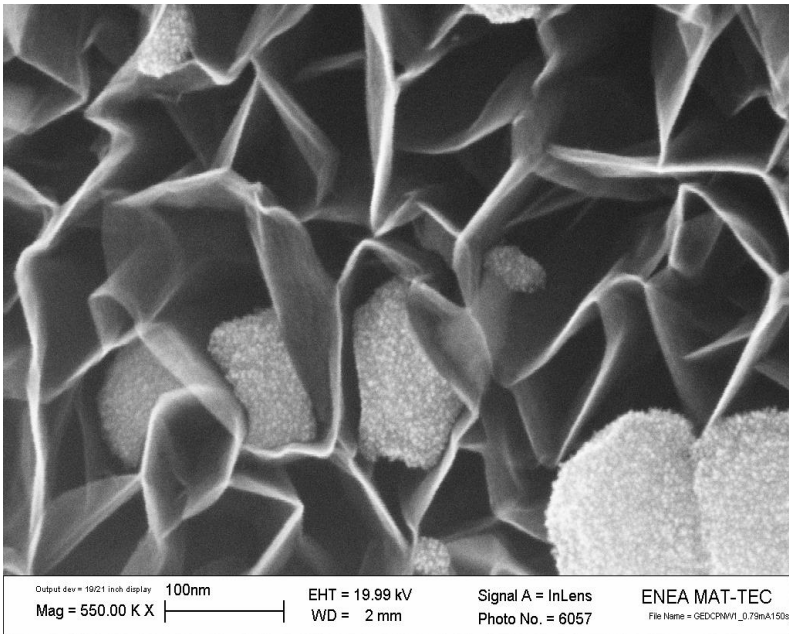
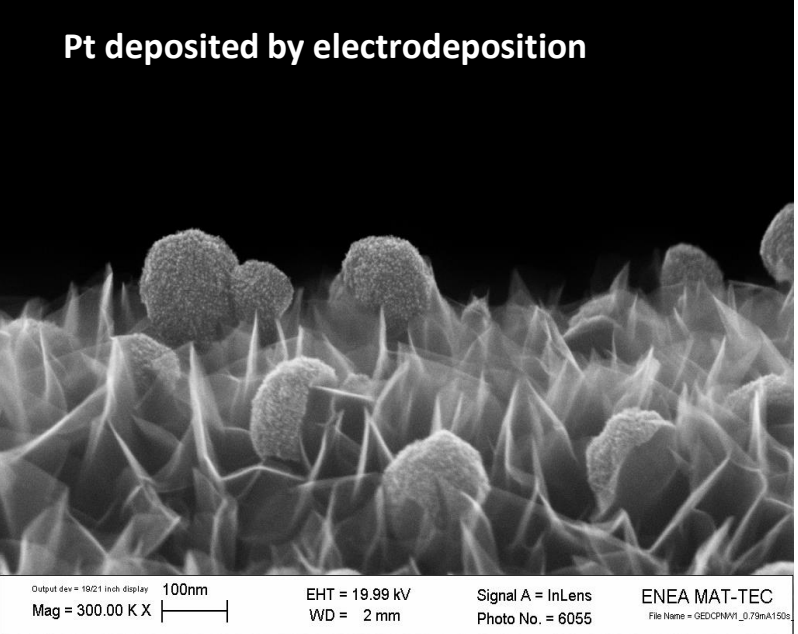


Mg Ka1_2

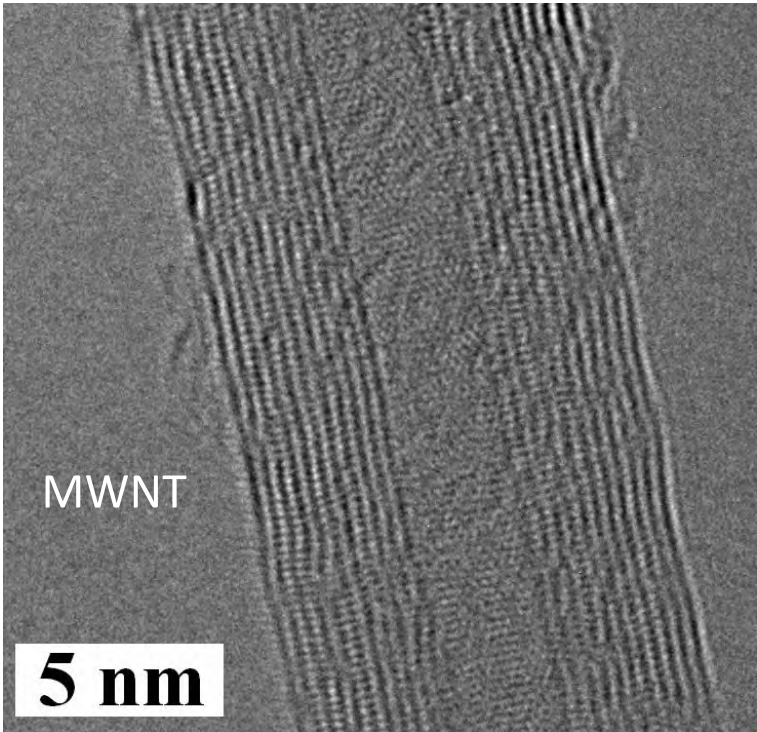
Some examples (SEM)



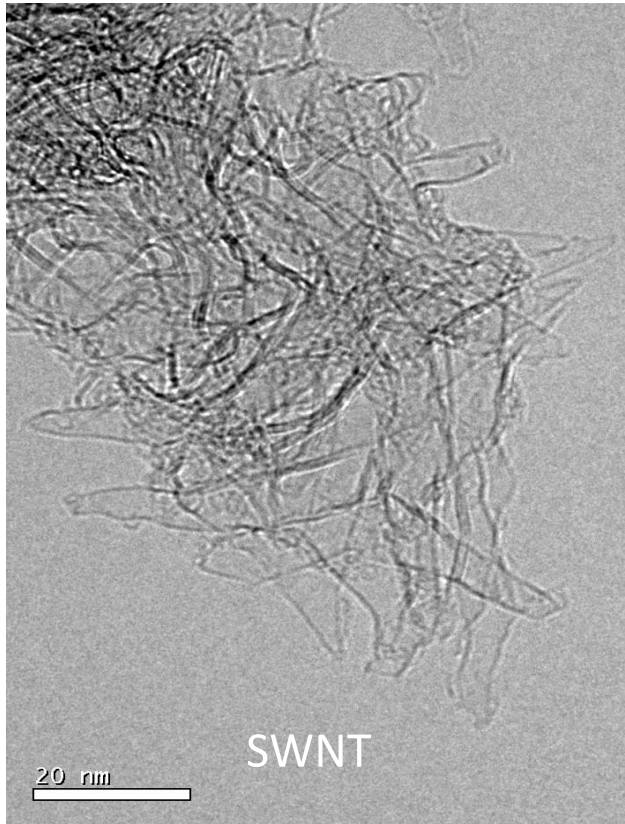
By using carbon nanostructures as high specific surface support for the catalyst, a better dispersion of the nanoparticles is obtained compared to traditional support (Vulcan CX-72R)



Some examples (TEM)

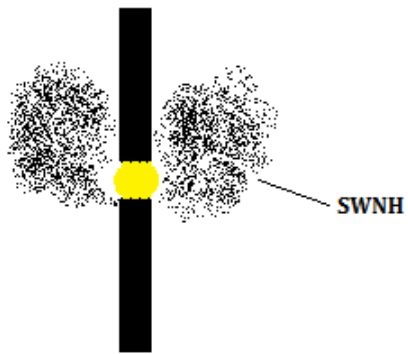
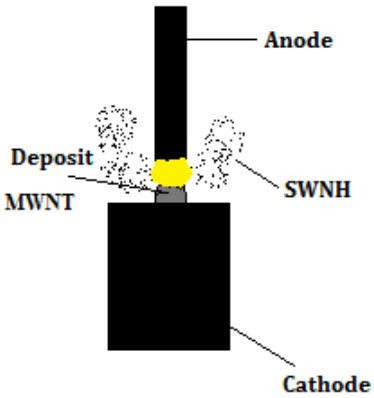


arc discharge in gaseous environments for synthesis of nano C structures



DC arc discharge

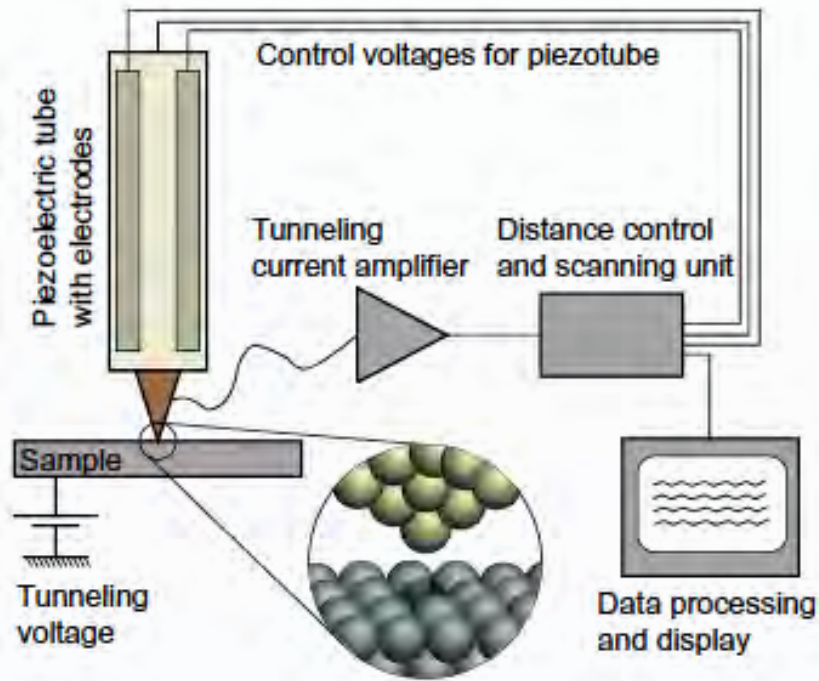
AC arc discharge



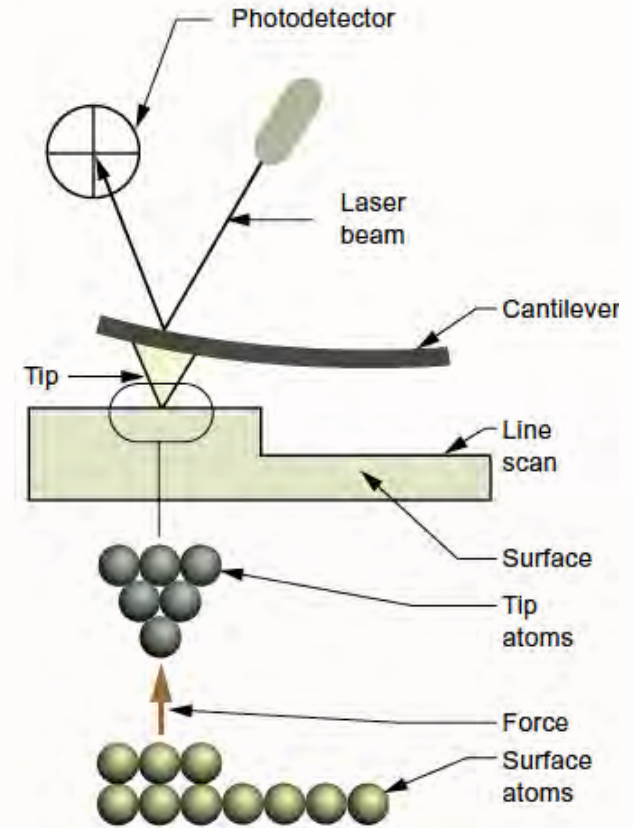
- D. Mirabile Gattia, M. Vittori Antisari, R. Marazzi, *Nanotechnology* 18 (2007) 255604
- M. Vittori Antisari, D. Mirabile Gattia, R. Marazzi, E. Piscopiello, A. Montone, *Mater. Res. Soc. Symp. Proc.* 1142 (2009) JJ05-16

Scanning Probe Microscopy

Scanning Tunneling Microscope (STM)



Atomic Force Microscope (AFM)

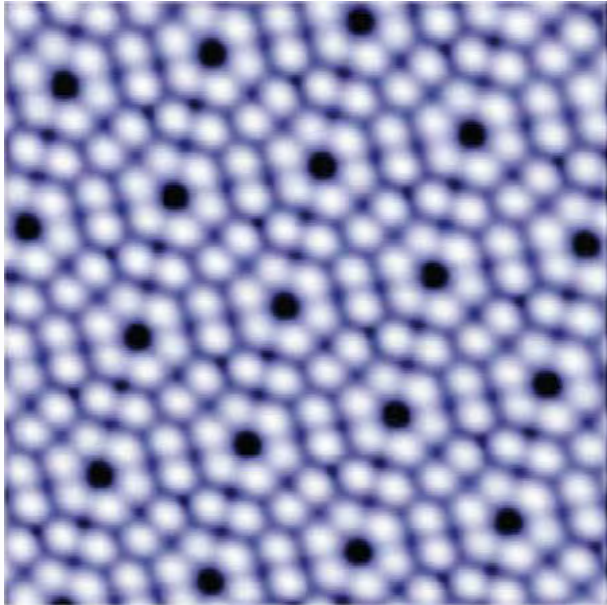


Scanning Probe Microscopy

the ability to monitor **very small** variations in topography.

Scanning Tunneling Microscope (STM)

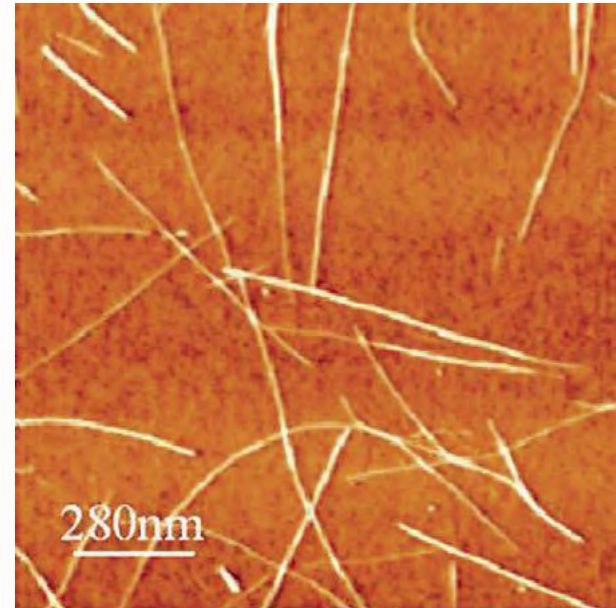
sub-angstrom vertical resolution
atomic lateral resolution



STM image of silicon (111)
7x7 surface reconstruction

Atomic Force Microscope (AFM)

atomic scale resolution



AFM image of carbon nanotubes

Analytical Techniques

kind of information

Chemical Composition

Chemical Bonding

electron

X-Ray Microanalysis

Electron Energy Loss Spectroscopy (EELS)

Infrared (IR) Spectroscopy
Raman Spectroscopy



vibrational
spectroscopy

light

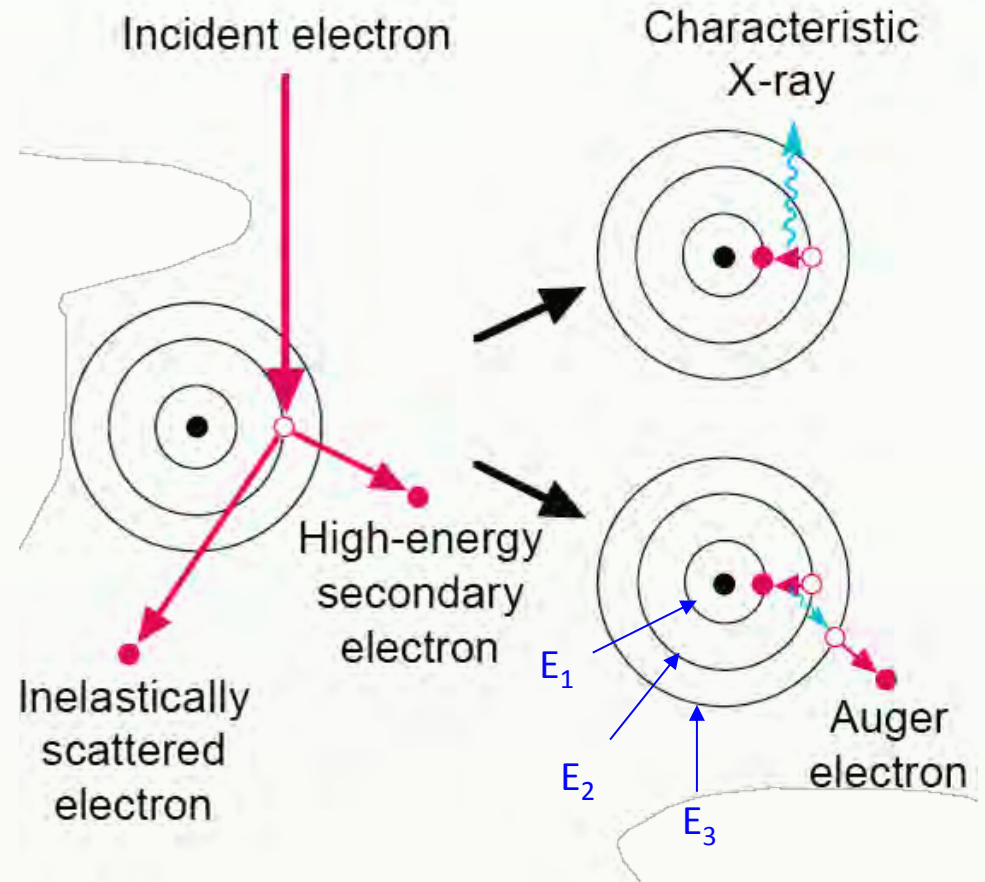
X-Ray Diffraction

Analytical Techniques

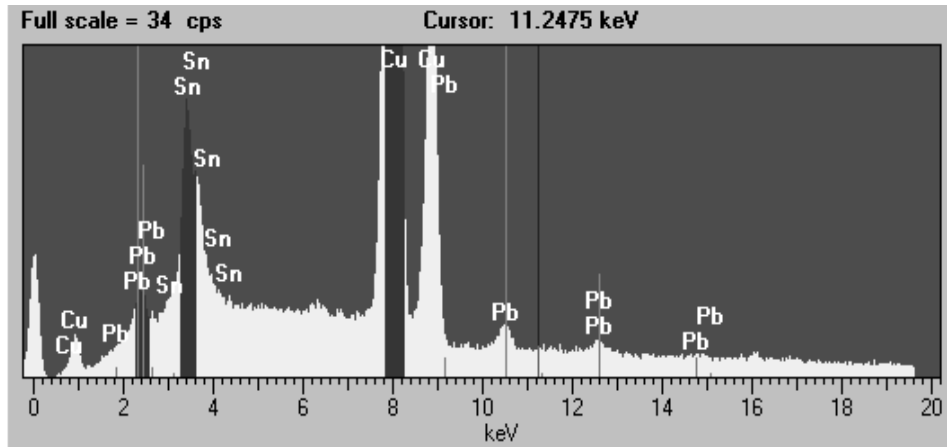
X-Ray Microanalysis

1. **Ionization** of electrons belonging to inner shells of atoms
2. **electrons decay** to their relaxed states
3. **X-rays are emitted** with energies unique to the ionized atom.

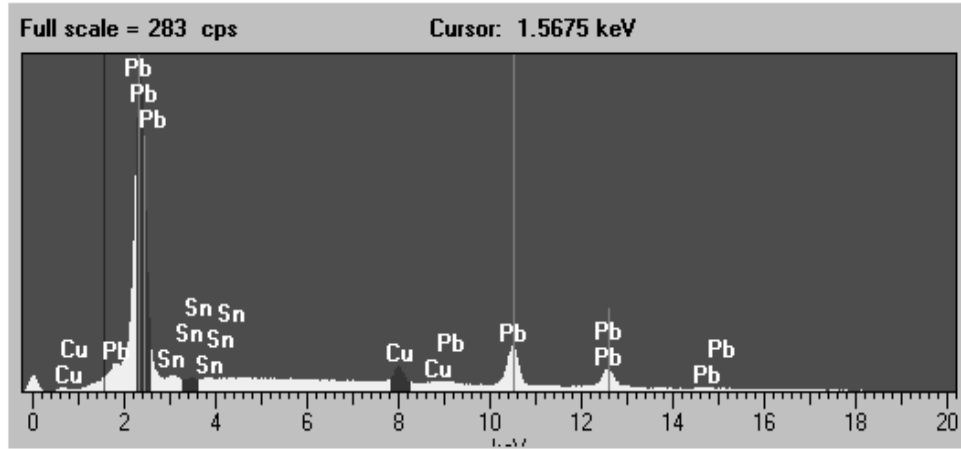
minimum detectability
0.1 at%



Some examples



GENERALE



PARTICELLA BIANCA

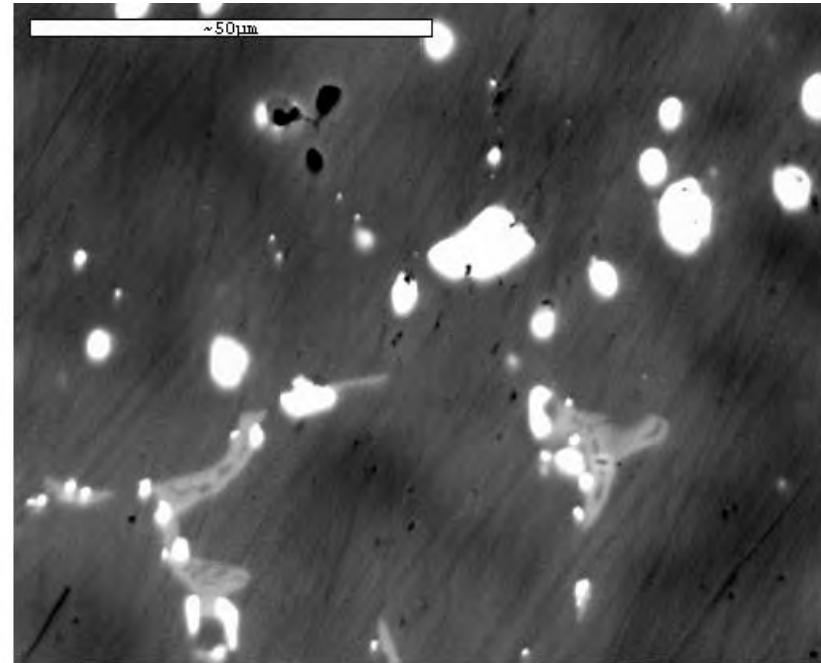
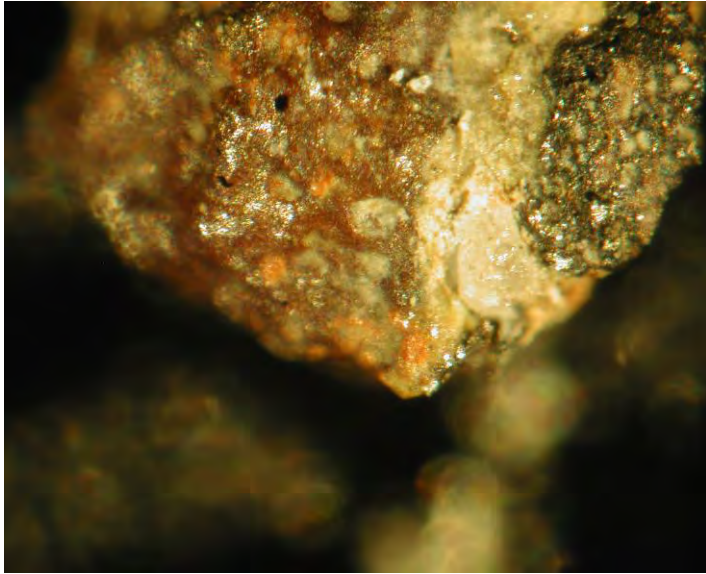
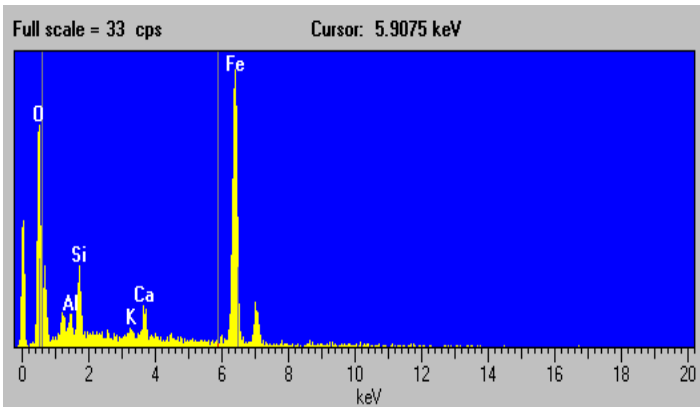
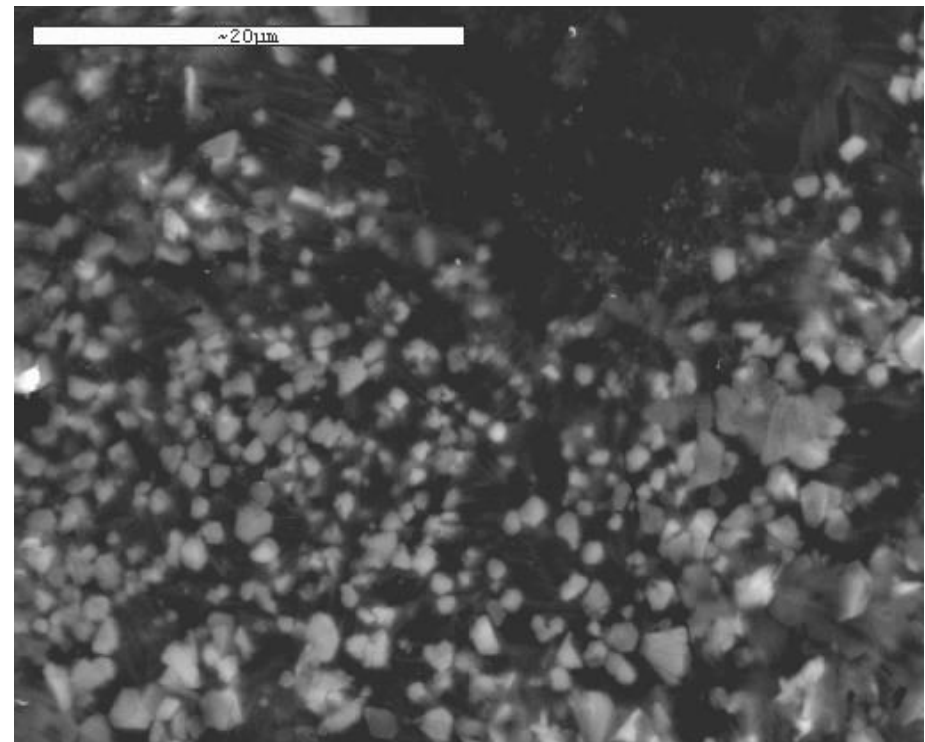
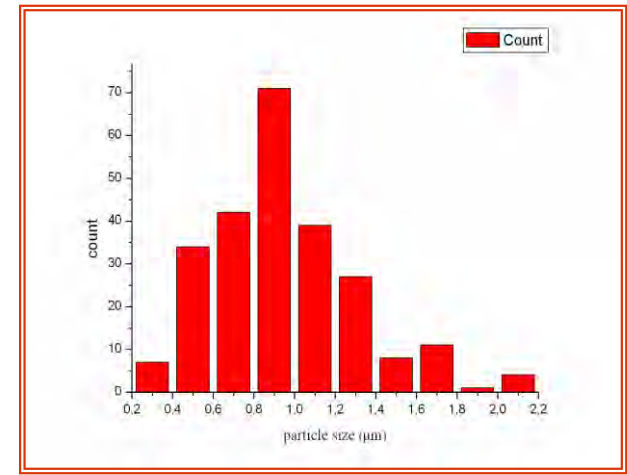


IMMAGINE BSE

Some examples

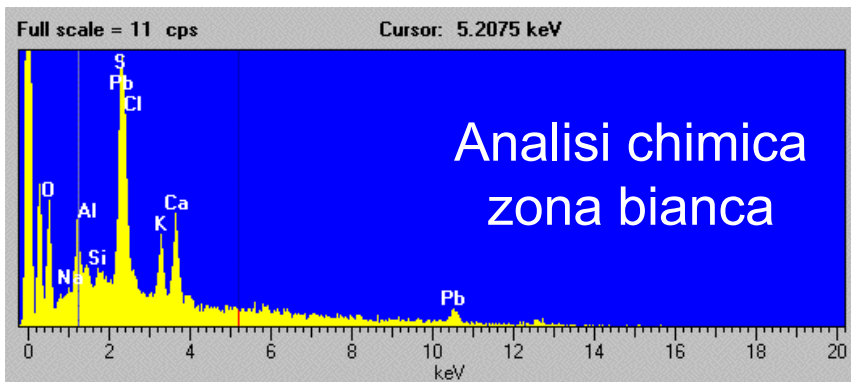
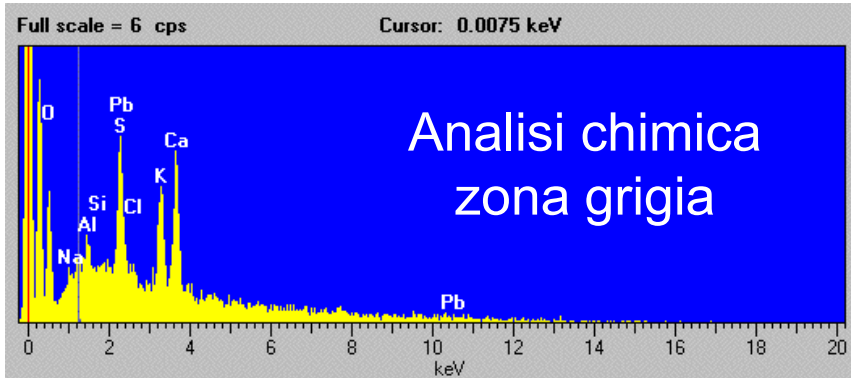
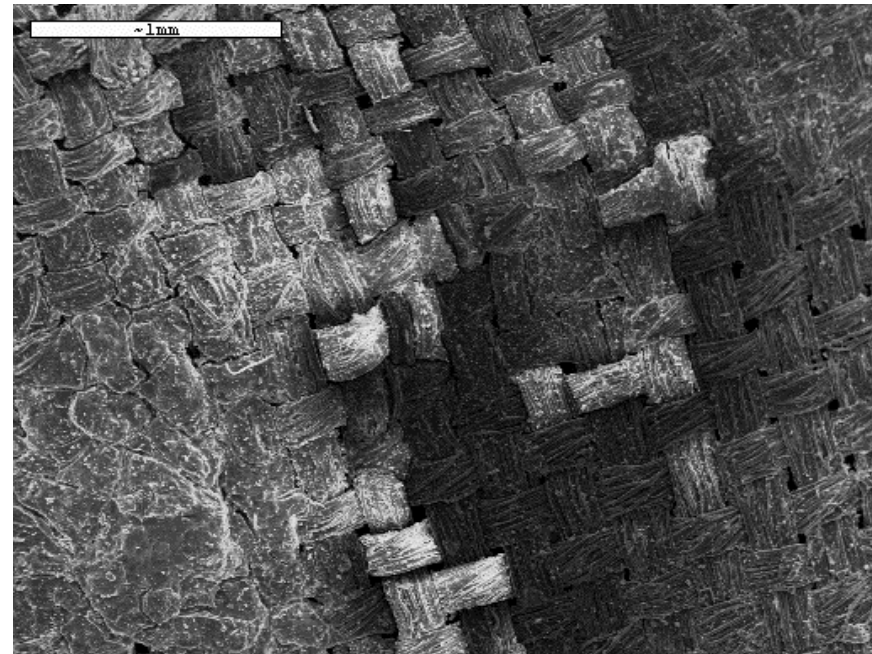
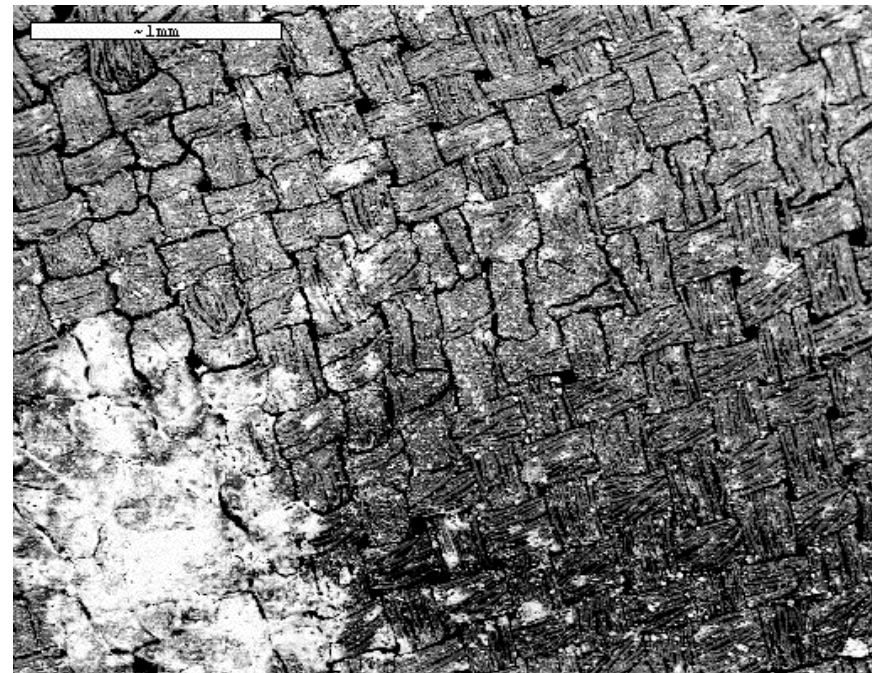


Apollo di Veio



Some examples

Mongolfiera Garnerin (anno 1804)



Analytical Techniques

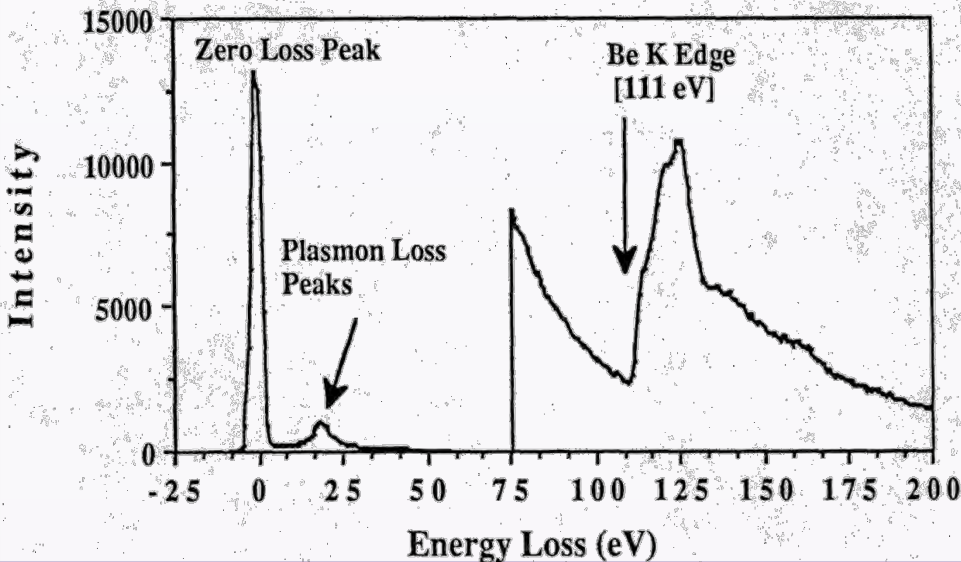
Electron Energy Loss Spectroscopy (EELS)

measure the energy loss of inelastic scattered electrons



atomic resolution chemical analysis
chemical bonding information

Width of zero-loss peak, typically 0.2–2 eV, reflects mainly the energy distribution of the electron source

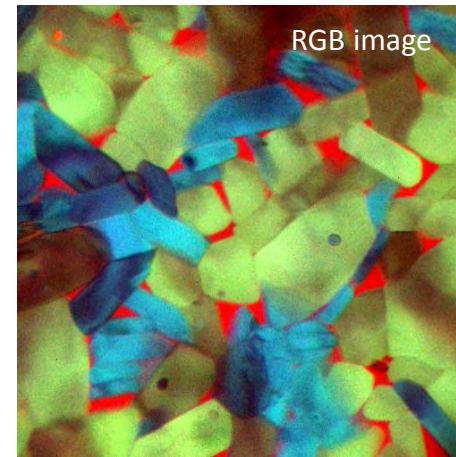
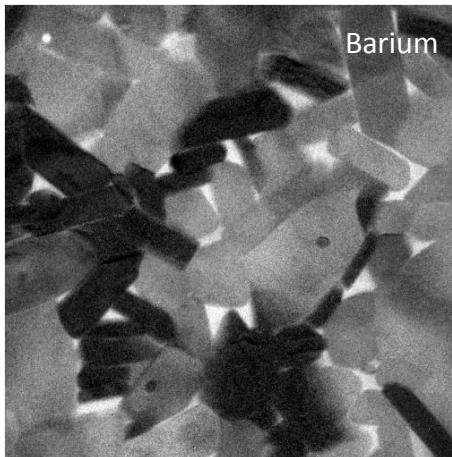
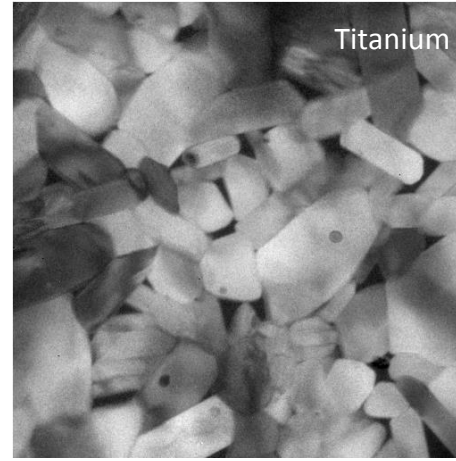
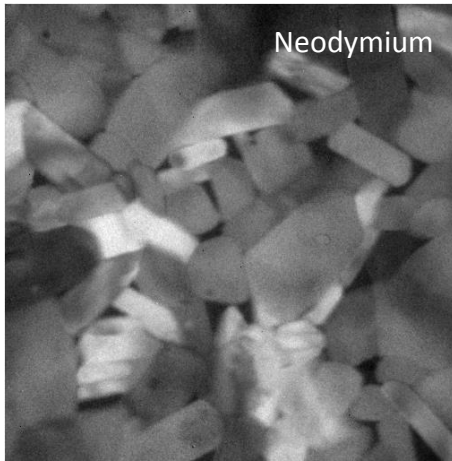


Atomic Number	Inner Shell	Spectroscopic Notation
Z = 1-11	K	1 s
Z = 12-17	K L ₃ ,L ₂ ,L ₁	1 s 2 p _{3/2} ,2 p _{1/2} ,2 s
Z = 19-45	L ₃ ,L ₂ ,L ₁ M ₅₄ ,M ₃₂ ,M ₁	2 p _{3/2} ,...-> 3 d _{5/2} ,3 d _{3/2} , 3 d _{1/2} , 3 p _{3/2} ,3 p _{1/2} ,3 s
Z = 46-79	M ₅₄ ,M ₃₂ ,M ₁ N ₄₅ ,N ₃₂ ,N ₁ O ₃₂ ,O ₁	3 d _{5/2} ,...-> 4 d _{5/2} ,4 d _{3/2} ,4 d _{1/2} , 4 p _{3/2} ,4 p _{1/2} ,4 s 5 p _{3/2} ,5 p _{1/2} ,5 s
Z > 80	N ₆₇ ,N ₄₅ ,N ₃₂ ,N ₁ O ₄₅ ,O ₃₂ ,O ₁	4 f _{7/2} ,...-> 5 p _{3/2} ,...->

Edges suitable for EELS
microanalysis for the energy
range
(0-3 keV)

Some examples

Elemental mapping



Ti Nd Ba

200nm

3 images/element using:

Nd M_{45} edge: @ 978 eV

Ti L_{23} edge: @ 455 eV

Ba M_{45} edge: @ 781 eV

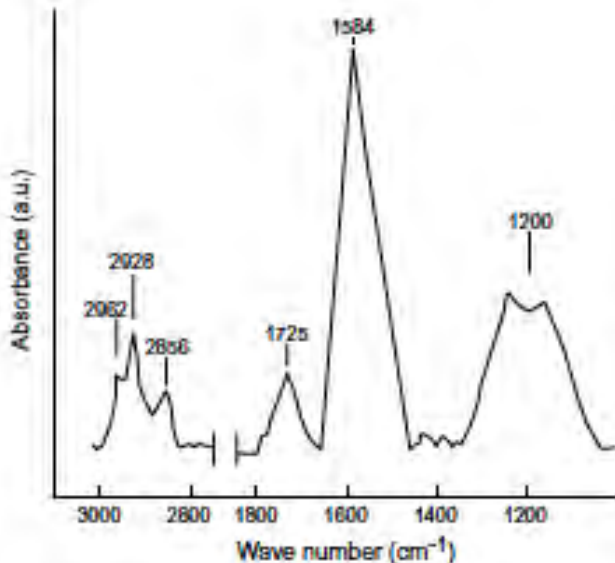
Color overlays, RGB images:

- assign a color to each elemental map: Ti green, Nd blue and Ba red
- Superimpose three color layers to form RGB composite
- shows chemical phase distribution qualitatively only

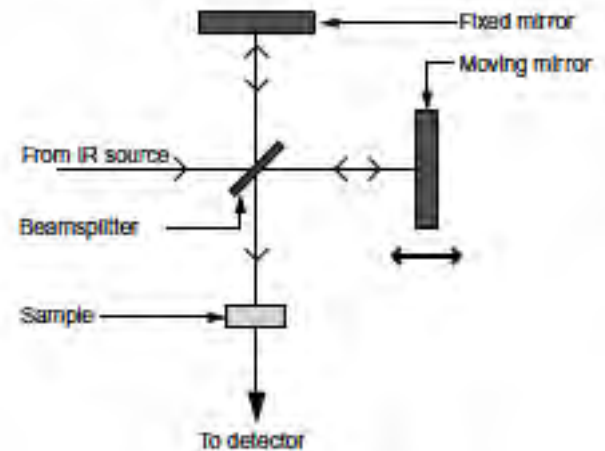
Analytical Techniques

infrared (IR) Spectroscopy

differences in the chemical and atomic structure of materials give rise to specific vibrational characteristics and yield **unique IR spectra for each material**.



Infrared spectrum of carbon nanotubes synthesized by chemical vapor deposition



In the case of nanomaterials is used to determine the extent of absorption of foreign species in nanoparticles of different sizes as well as the structure of nanorods, nanowires, and carbon nanotubes

Analytical Techniques

Raman spectroscopy

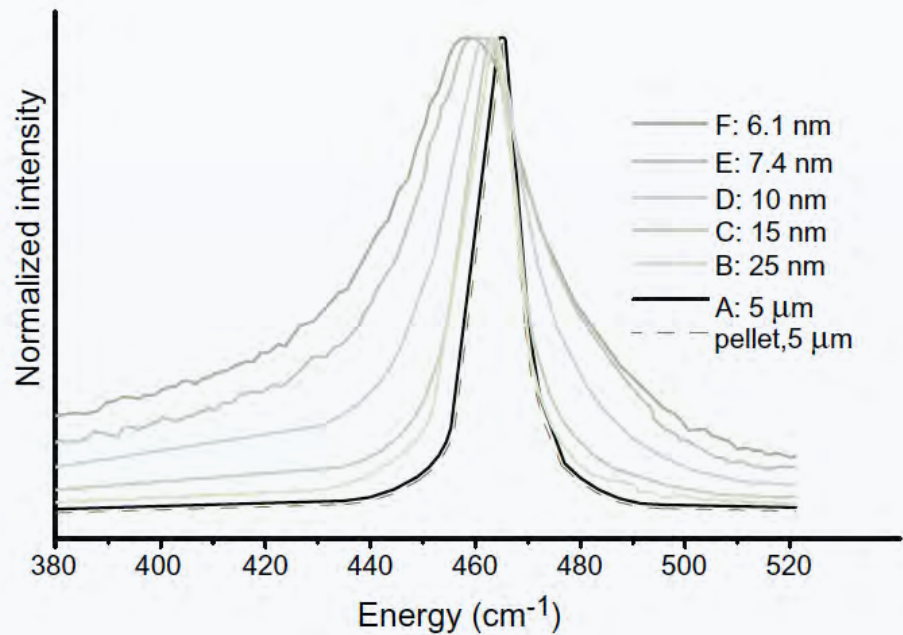
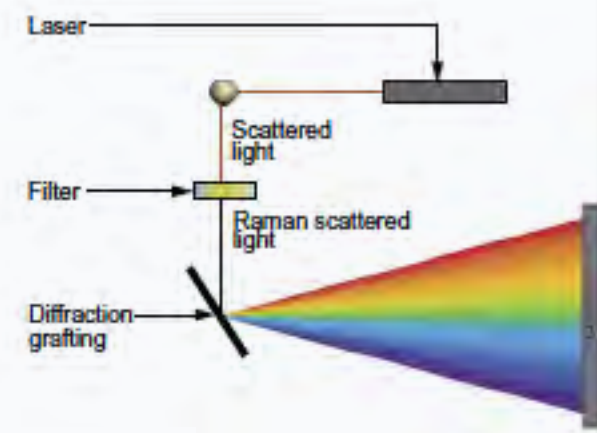
Complementary to IR spectroscopy: some vibrational modes IR-active, others Raman-active

extensively used for CN:

their mode frequencies are a function of size and chirality

changes in nanoparticle size:

Raman spectrum tends to broaden and shift to lower frequencies as the particle size decreases



Size-dependent properties of CeO₂- γ nanoparticles by Raman scattering

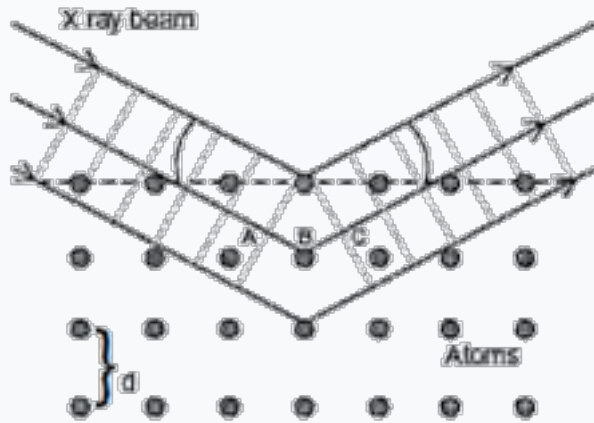
Analytical Techniques

X-ray Diffraction

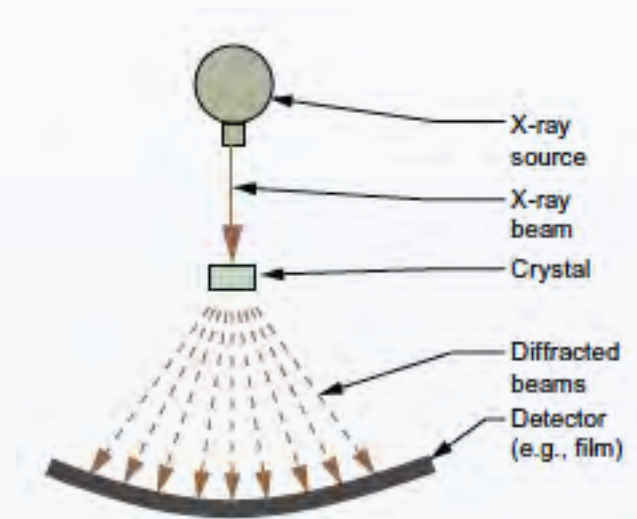
peak intensity depends on

- **structure factor**, which is related to the position of atoms within the unit cell
- **shape factor**, and it is related to the size of the crystal

Bragg's law of diffraction.

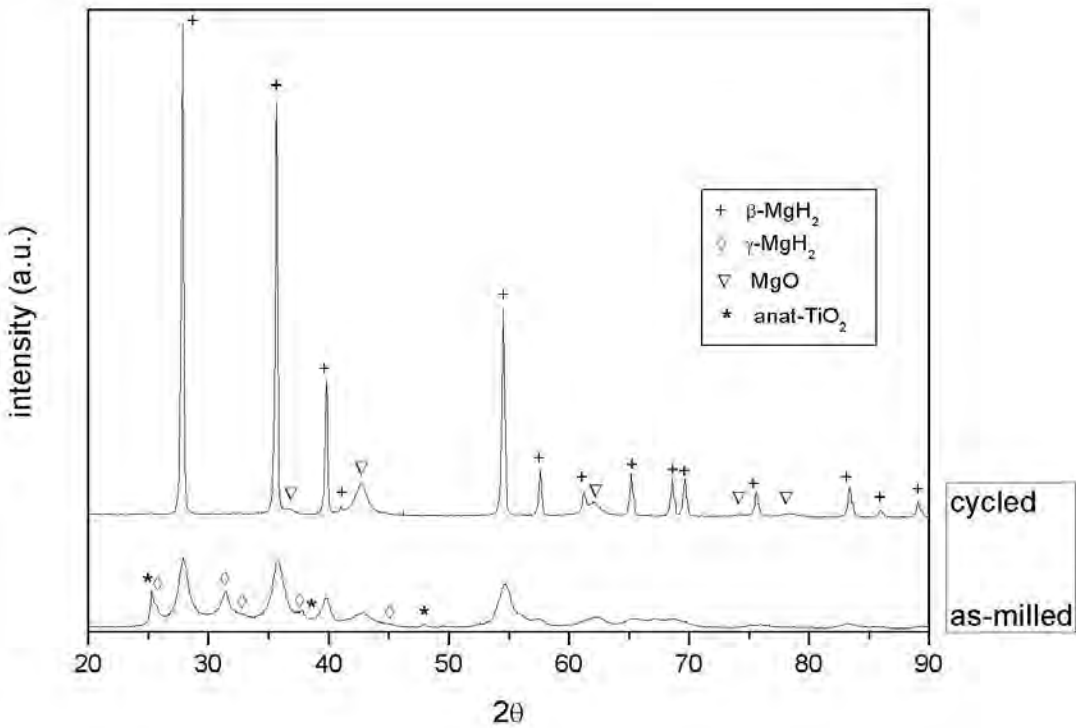


$$2d \sin \alpha = n\lambda$$



schematic X-ray diffractometer

Some examples



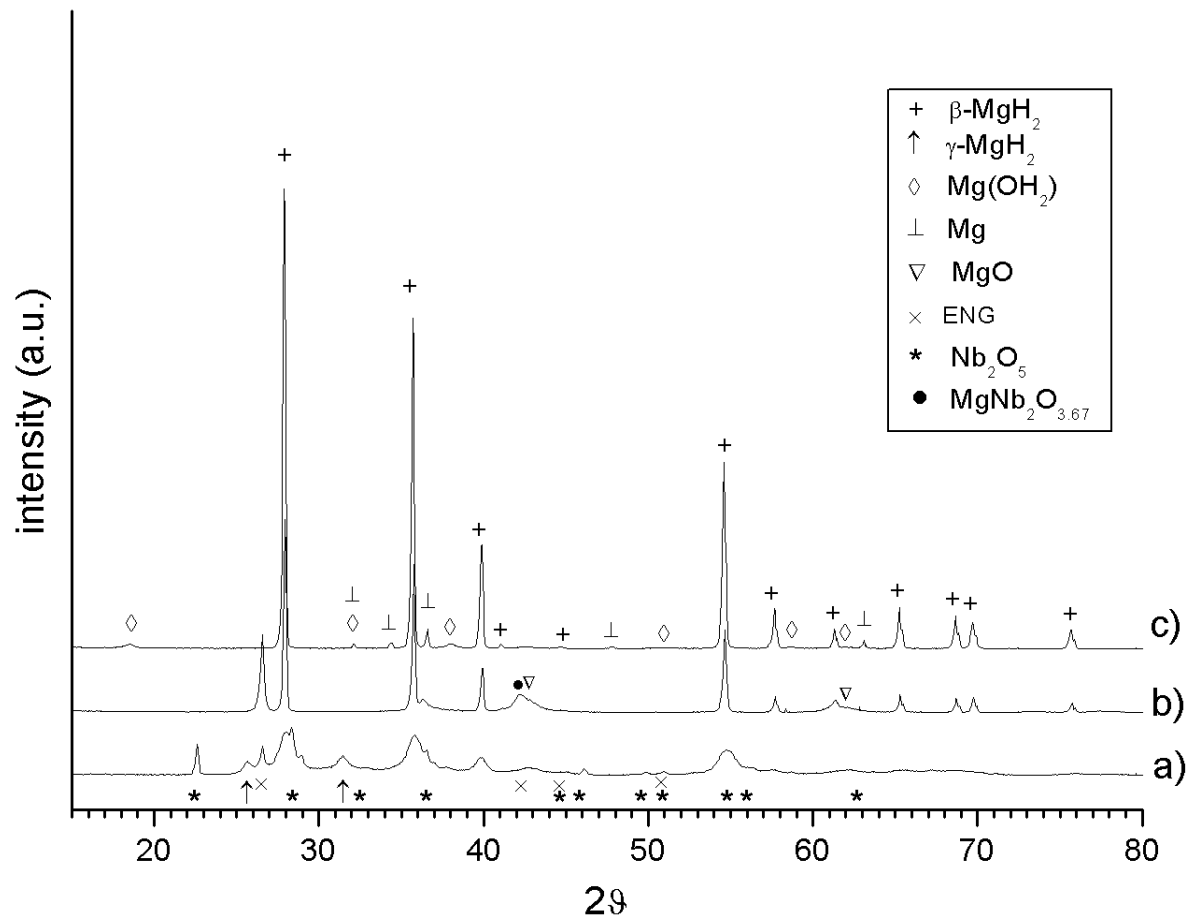
Sample:
MgH₂ + 5wt%TiO₂ + 5wt% ENG

Cycling Parameters:
340° C – 1.2bar/8bar

Rietveld analysis

			TiO ₂ anatase	β-MgH ₂	γ-MgH ₂	MgO
As milled	Cell parameters (nm)	a	0,37965	0,45279	0,45386	0,42325
		b	-	-	0,54326	-
		c	0,95381	0,30292	0,49705	-
	Crystallite size (nm)		181	10	8	11
<hr/>						
Cycled	Cell parameters (nm)	a	-	0,45085	-	0,42286
		b	-	-	-	-
		c	-	0,30239	-	-
	Crystallite size (nm)		-	157	-	10

Some examples

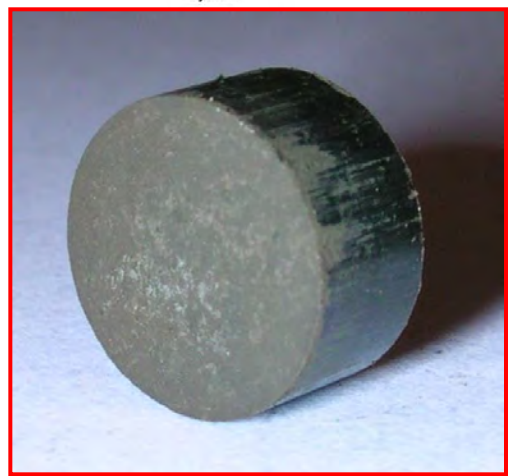
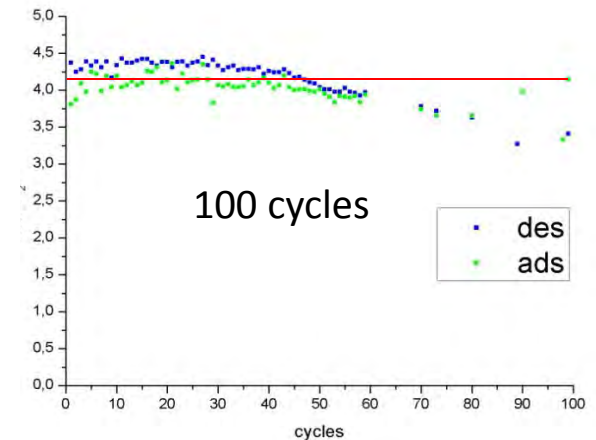


a) as milled MgH_2 with Nb_2O_5 and ENG
 b) pellet exposed to air after cycling, after complete absorption run
 c) MgH_2 as purchased

- Cycled sample:
- Mg-Nb-O ternary oxide is formed
 - Nb_2O_5 crystalline phase is not present
 - $Mg(OH)_2$ crystalline phase is absent

Sample:
 $MgH_2 + 10wt\%Nb_2O_5 + 5wt\% ENG$

Experimental conditions
 Desorption: 1.2 bar – 310 ° C
 Adsorption: 4 bar – 310 ° C
 After 2h air exposure



Thank for your
attention!

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