# Síntesis de sistemas nanoestructurados y su observación por técnicas de microscopia electrónica de Transmisión

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**Día Virtual de Microscopía**

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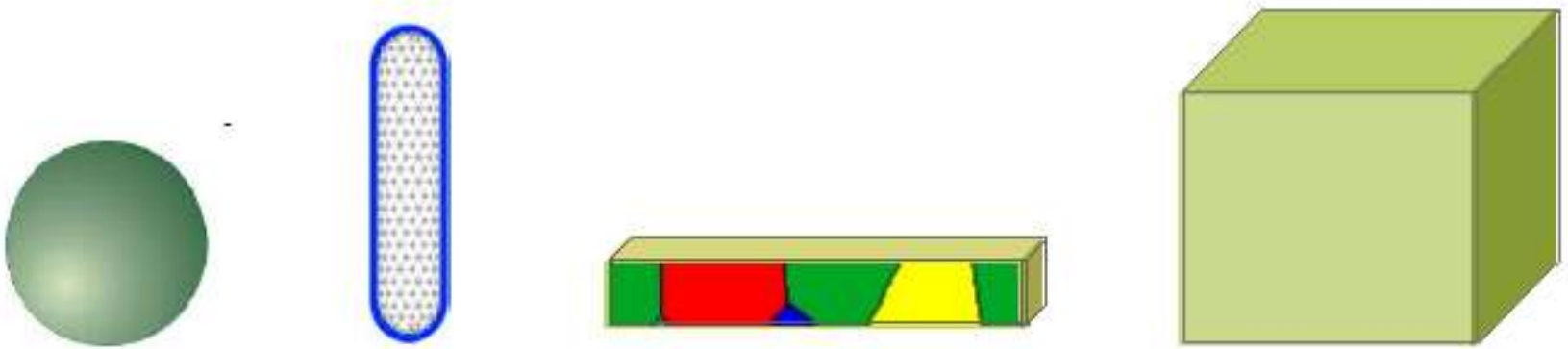
# Dimensions

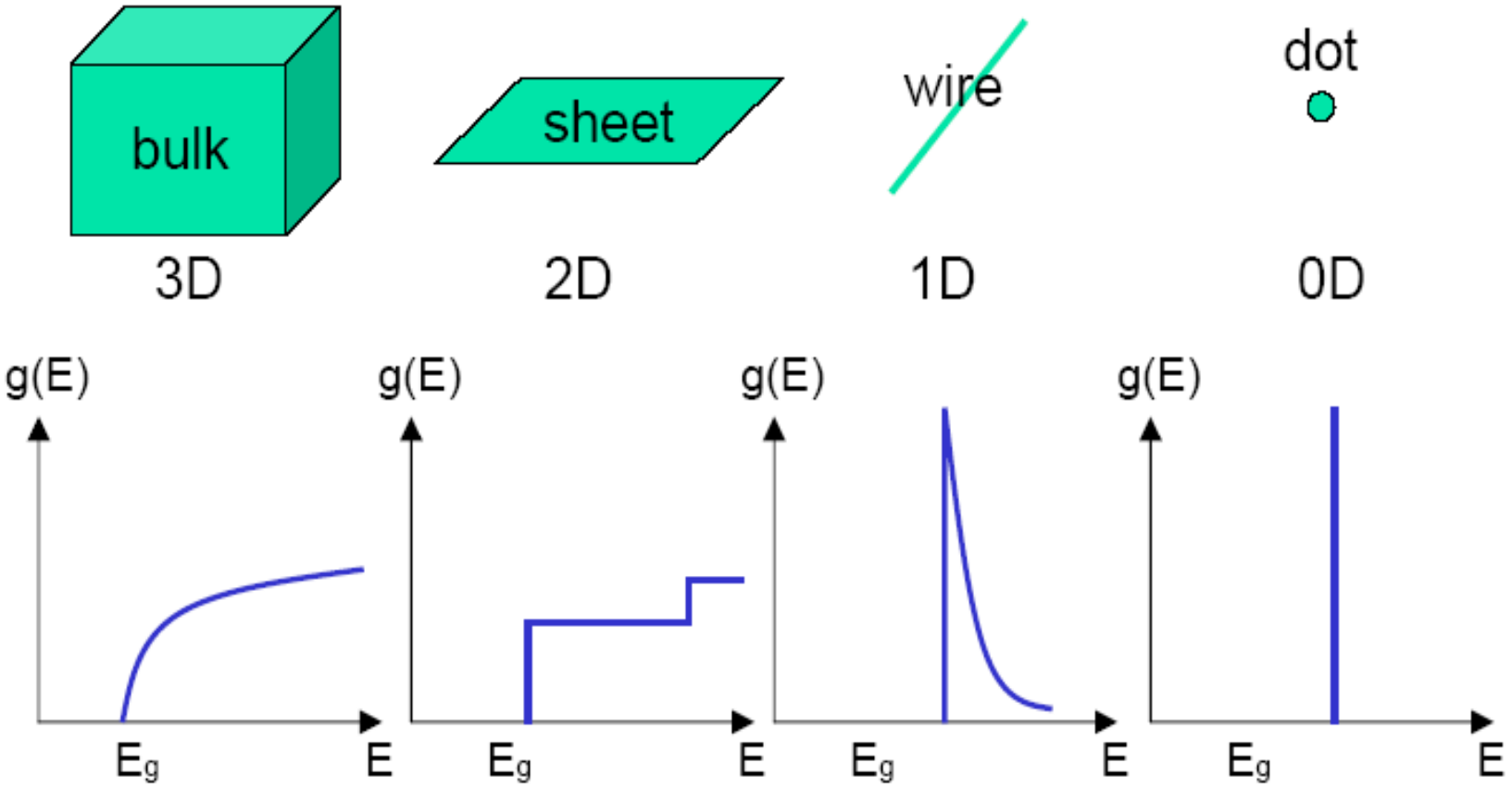
- **Nanoscale materials:**
  - Nanometer-sized entities (particles, clusters, grains, etc.) with unique new properties
- **Nanophase materials:**
  - "conventional" materials with nanometer-sized clusters, particles, crystallites, etc. to improve the overall 'macroscopic' performance
- **Dimension (modulation dimensionality):**

| 0D | 1D | 2D | 3D |
|---|---|---|---|
| nanoparticles | nanotubes/wires | nanolayers | nanophase materials |



# Electronic states

g(E) = Density of states



# HRTEM Characterization

TEM image formation

- HRTEM (Coherent image formation)
- HAADF-HR (Incoherence formation)
- Diffraction
- ADF-TDS
- Electron Holography
- EELS

# Electron Probe (Field Emission Gun)

## ~ 0.2 - 1 nm

S
E
M

T
E
M

**X-rays/Auger:**
*Chemistry*

**CL:**
*Light*

**Secondary Electrons** (SE)
*Image*

**Backscattered Electrons**(BSE)
*Image*

**50 - 100 nm**

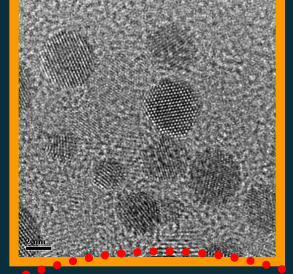
**Specimen Current/Heat**

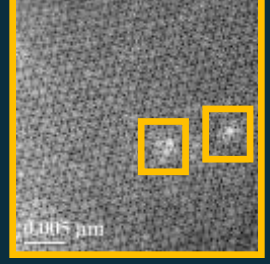
**Diffraction**:
*Structure/Crystallography*

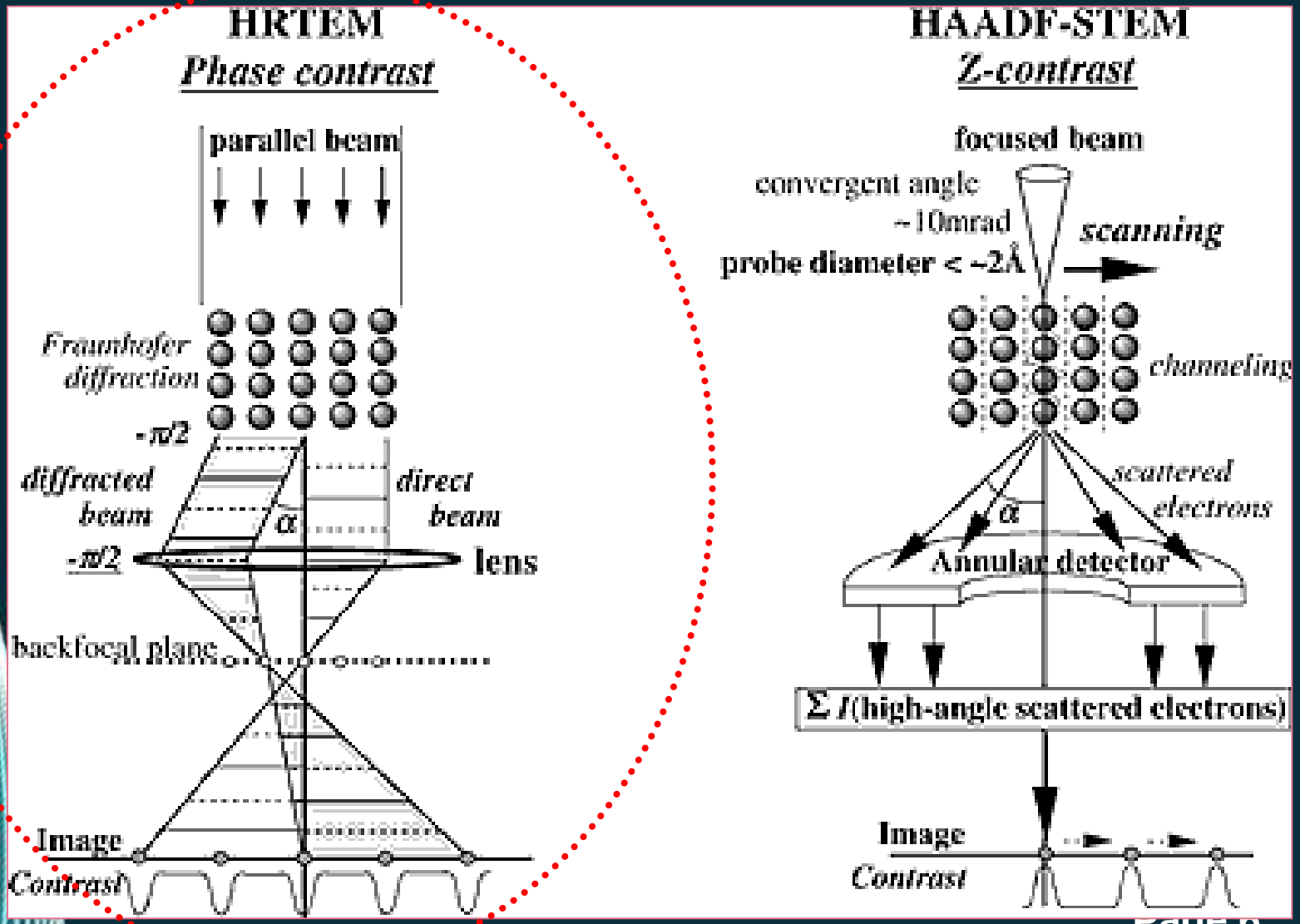
**BF/DF Imaging**

**TDS**:
*Z-contrast*

**E+/-ΔE**:
*Electronic Structure*

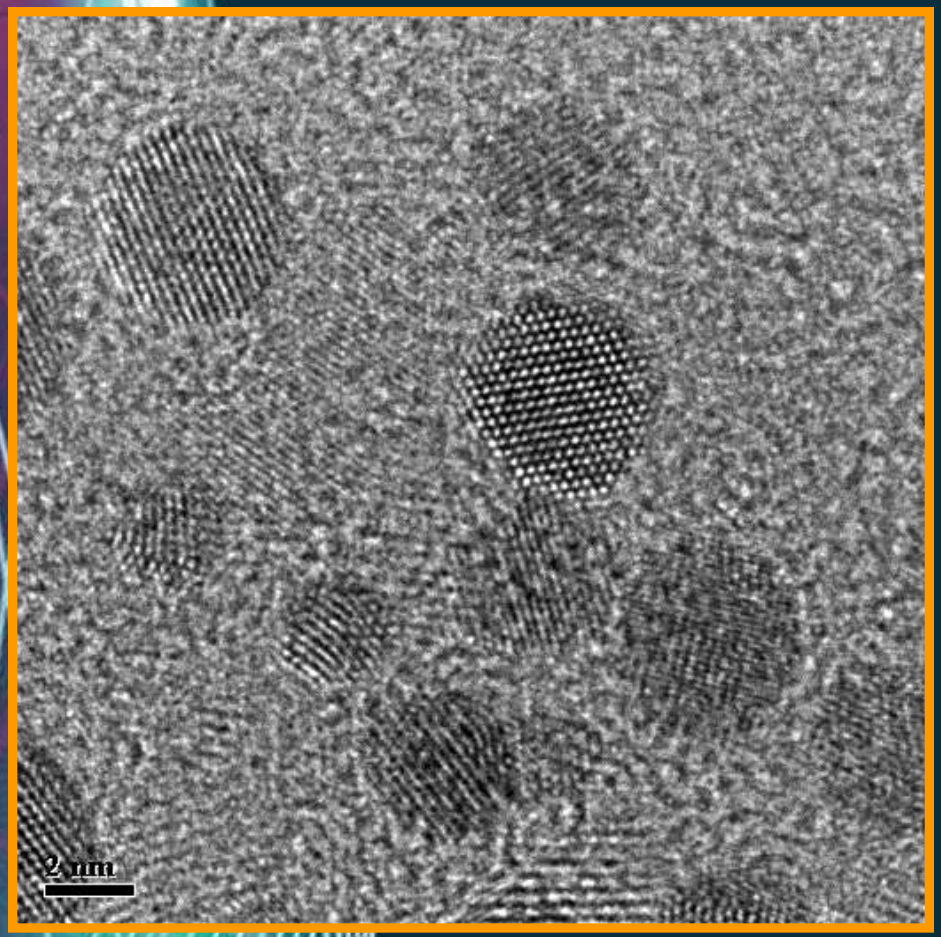




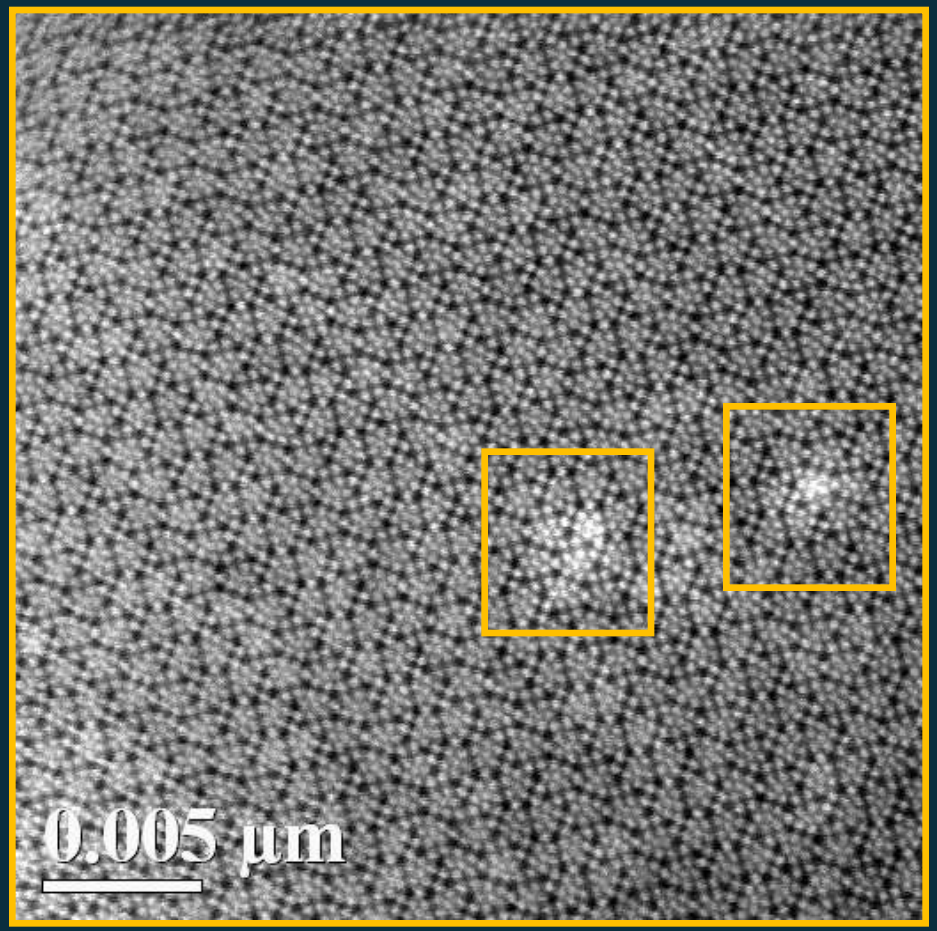

HRTEM
Phase contrast
parallel beam
Fraunhofer diffraction
-π/2
diffracted beam
direct beam
α
-π/2
lens
backfocal plane
Image
Contrast
HAADF-STEM
Z-contrast
focused beam
convergent angle
~10mrad
probe diameter < ~2Å
scanning
channeling
scattered electrons
α
Annular detector
Σ I(high-angle scattered electrons)
Image
Contrast

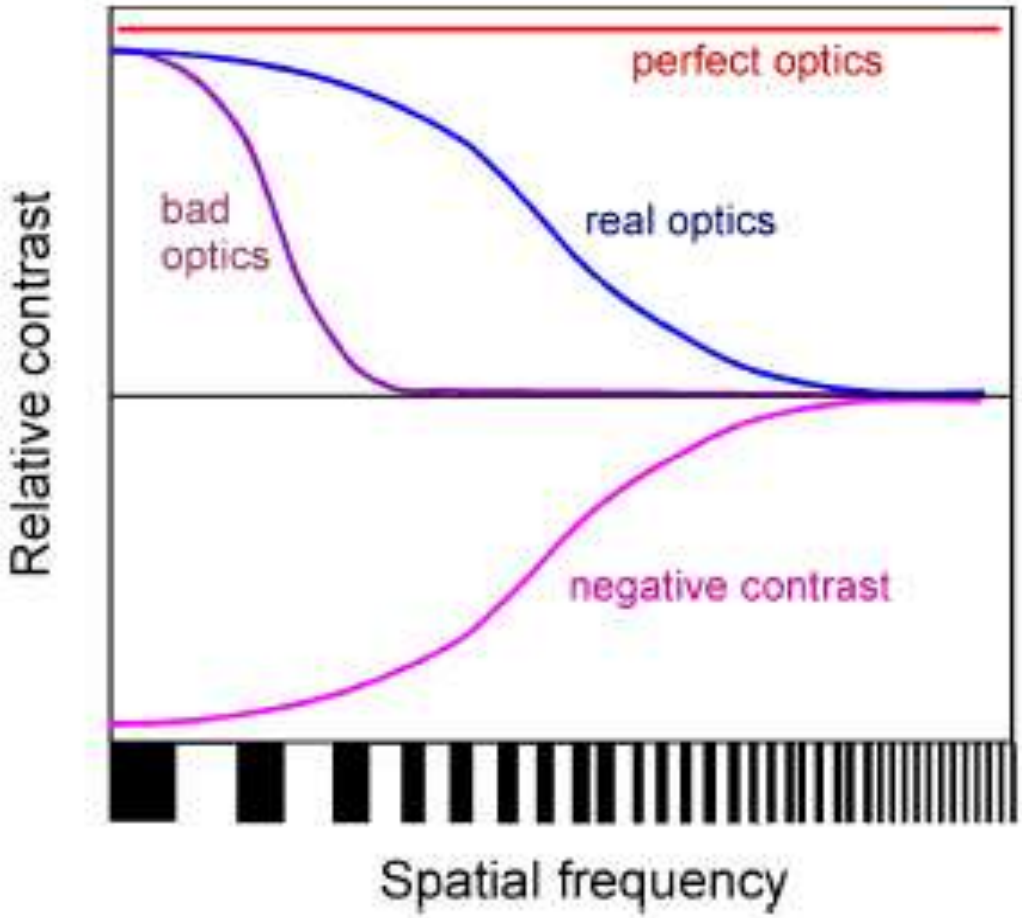
# HRTEM IMAGES

Coherence Image: Conventional TEM



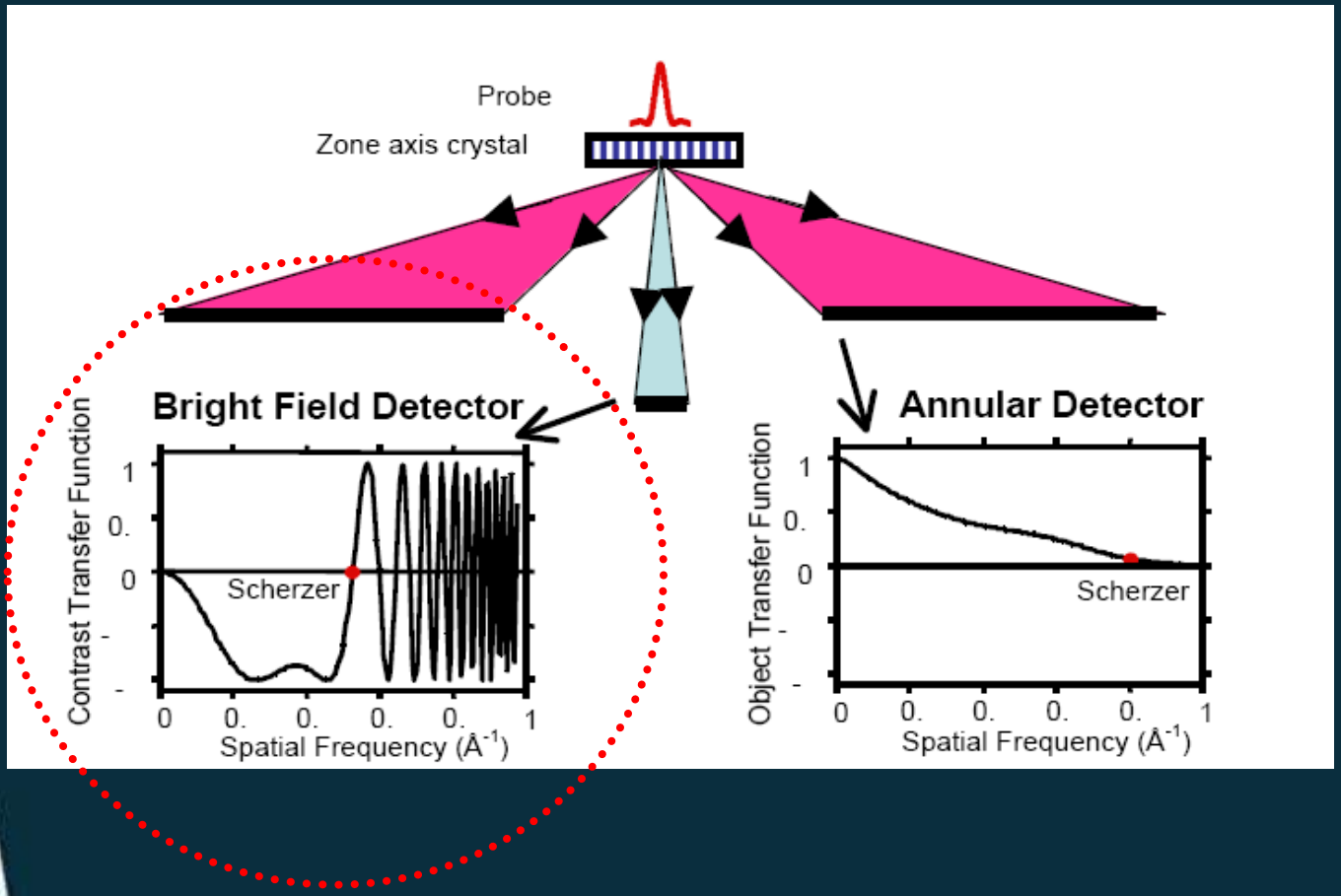

Incoherence Image: Z-Contrast



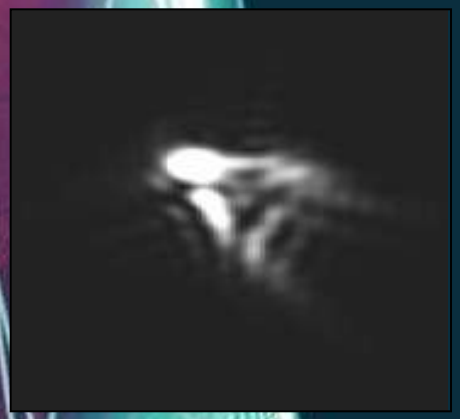

perfect optics
real optics
bad optics
negative contrast
Relative contrast
Spatial frequency


perfect optics
normal optics
bad optics
negative contrast

# Contrast Transfer Function

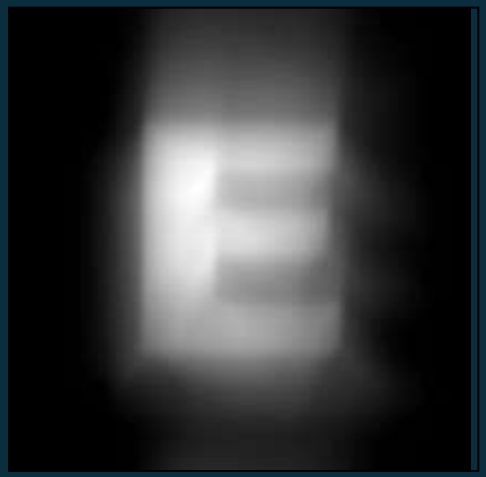


# Transfer Contrast Function



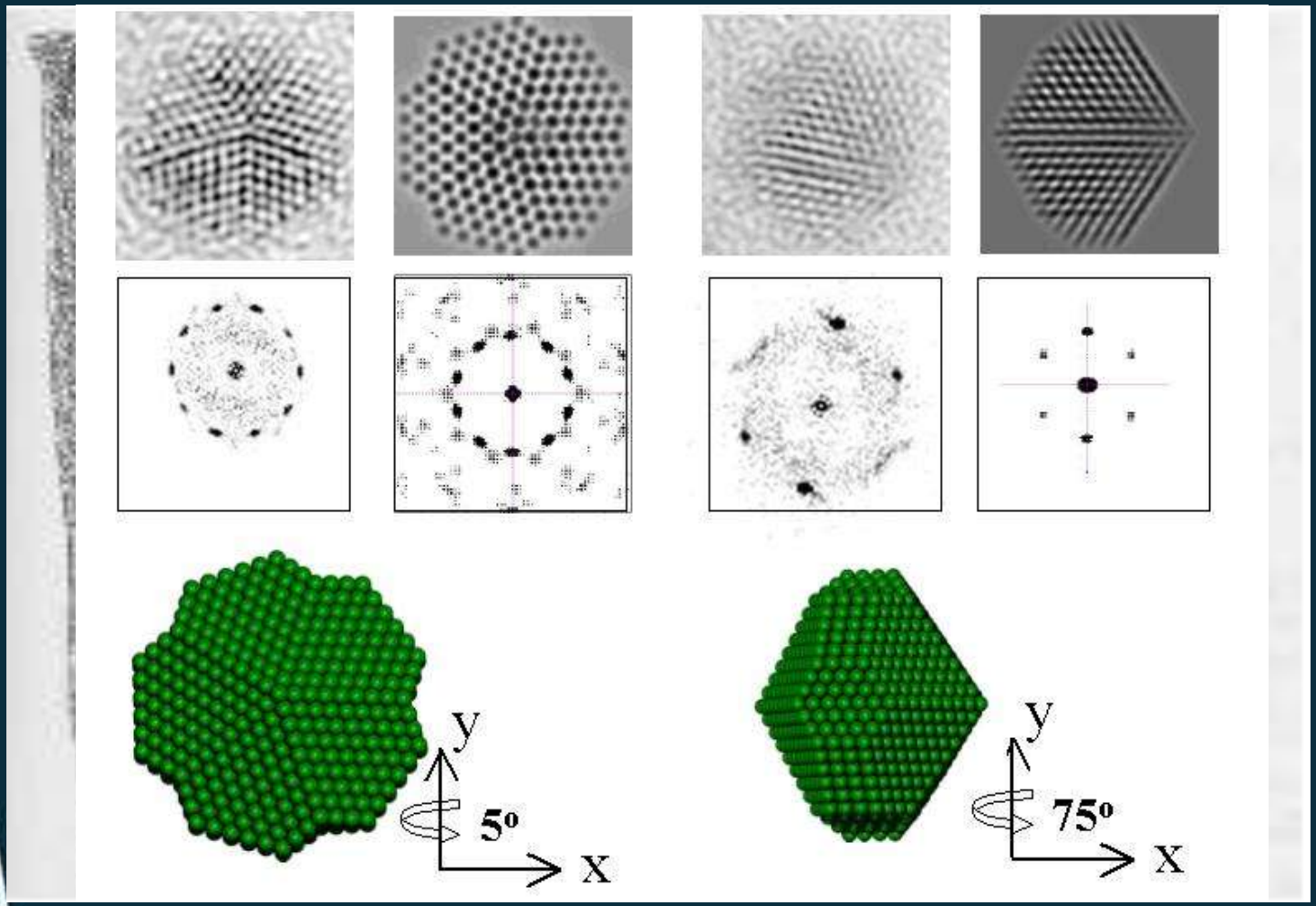
$\otimes$

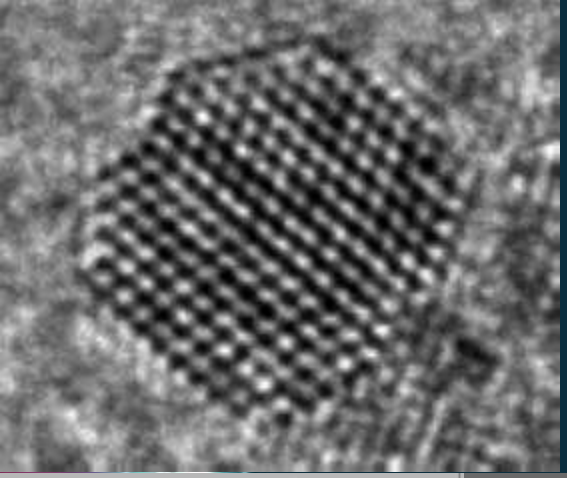
$=$

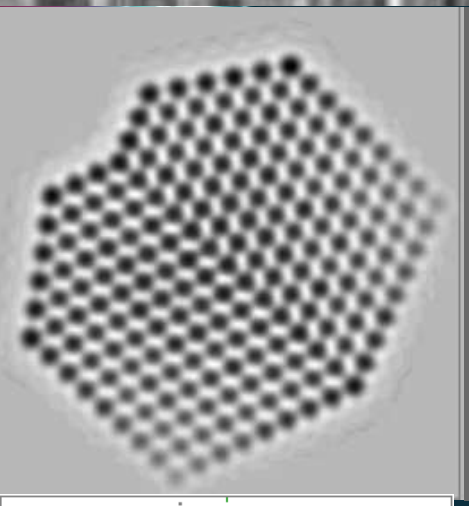


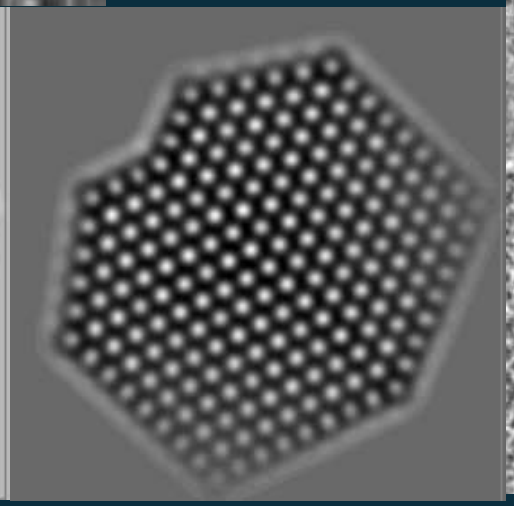
$$TF^{-1}\left[TF\left(T(r)\otimes O(r)\right)\right]=TF^{-1}\left[T(u)O(u)\right]=I(r)$$

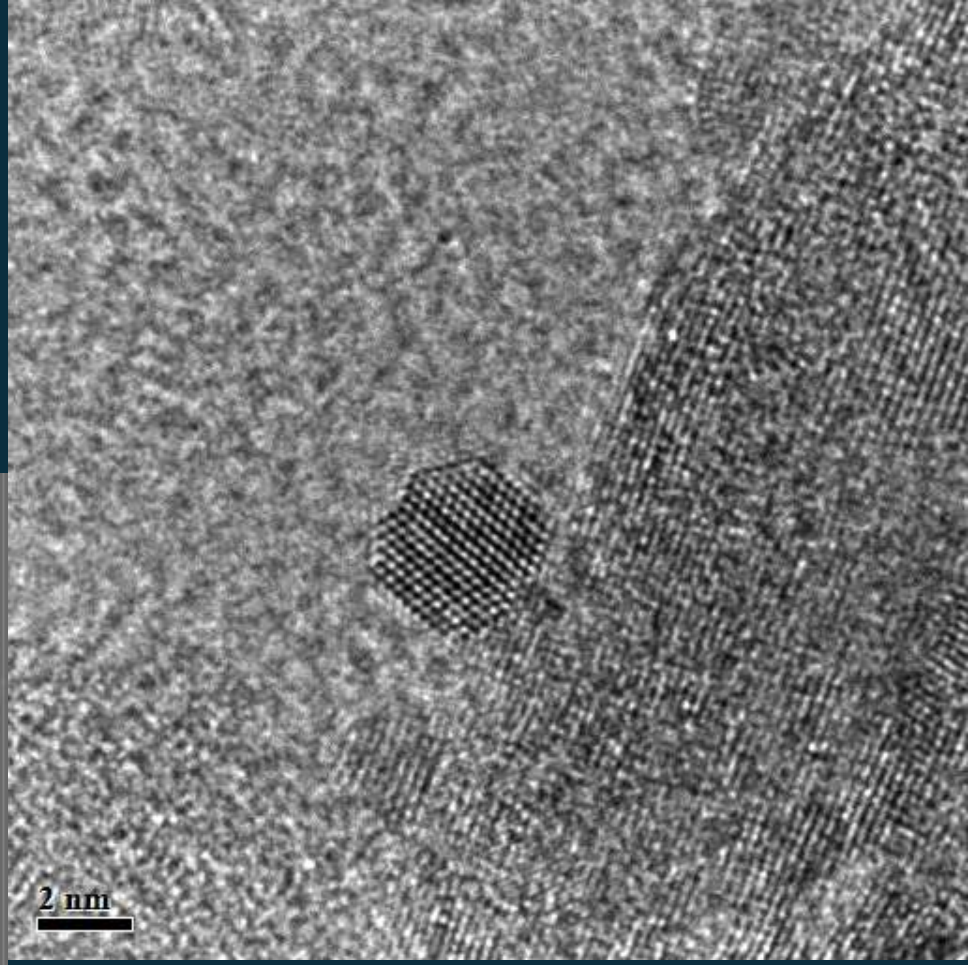
# Coherence atomic high resolution transmission electron microscopy images



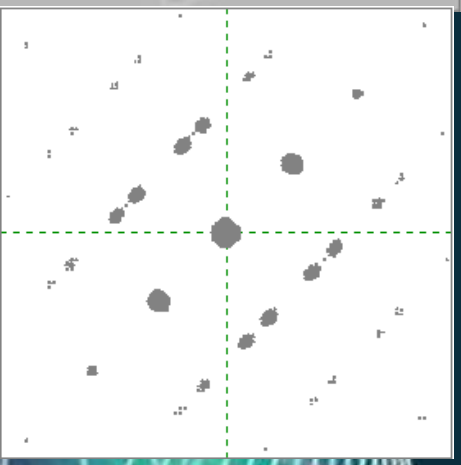


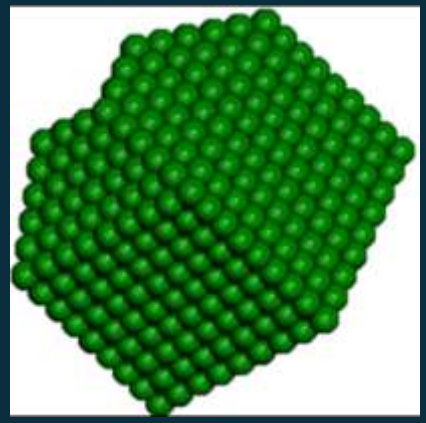


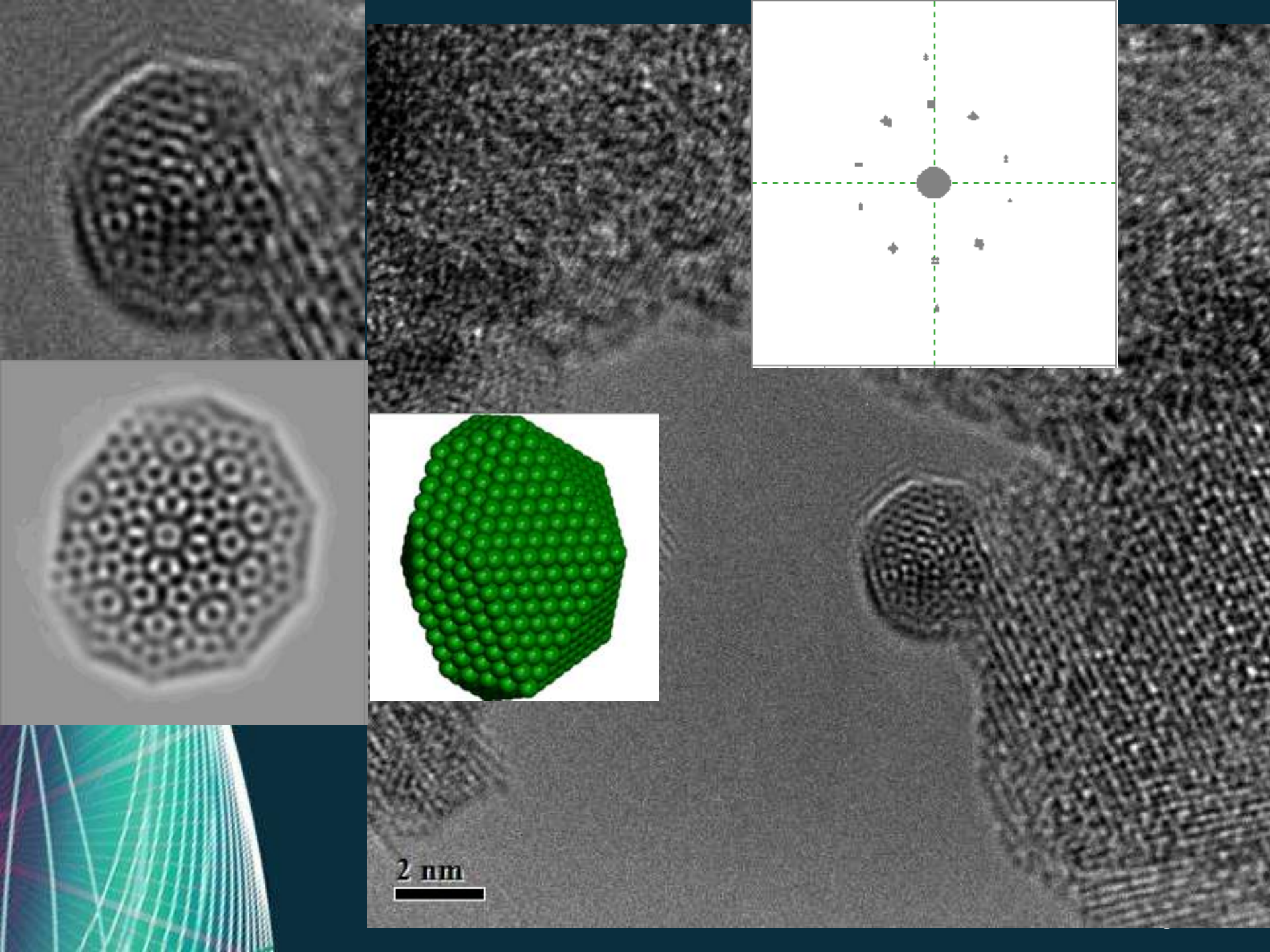


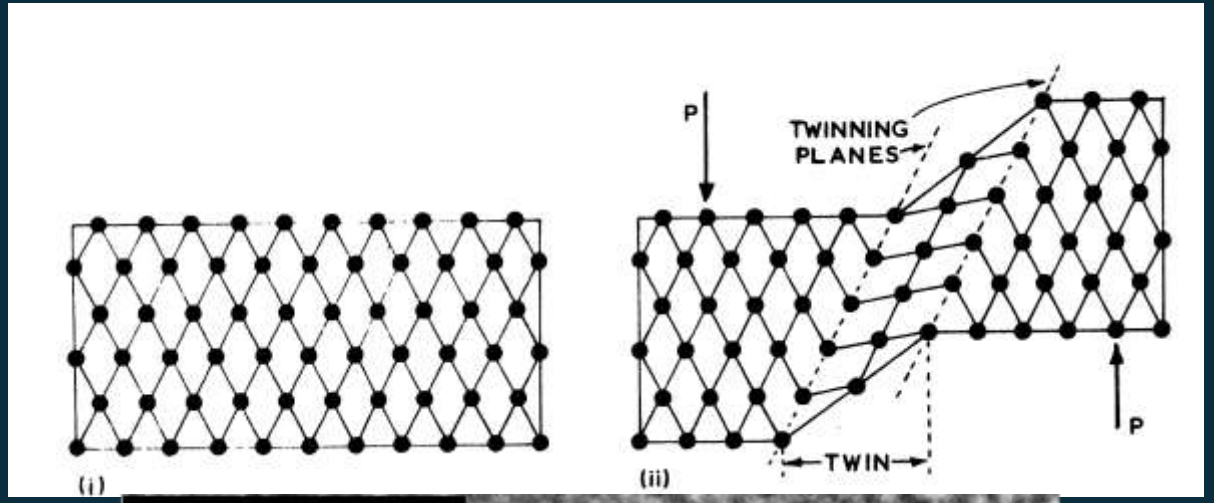


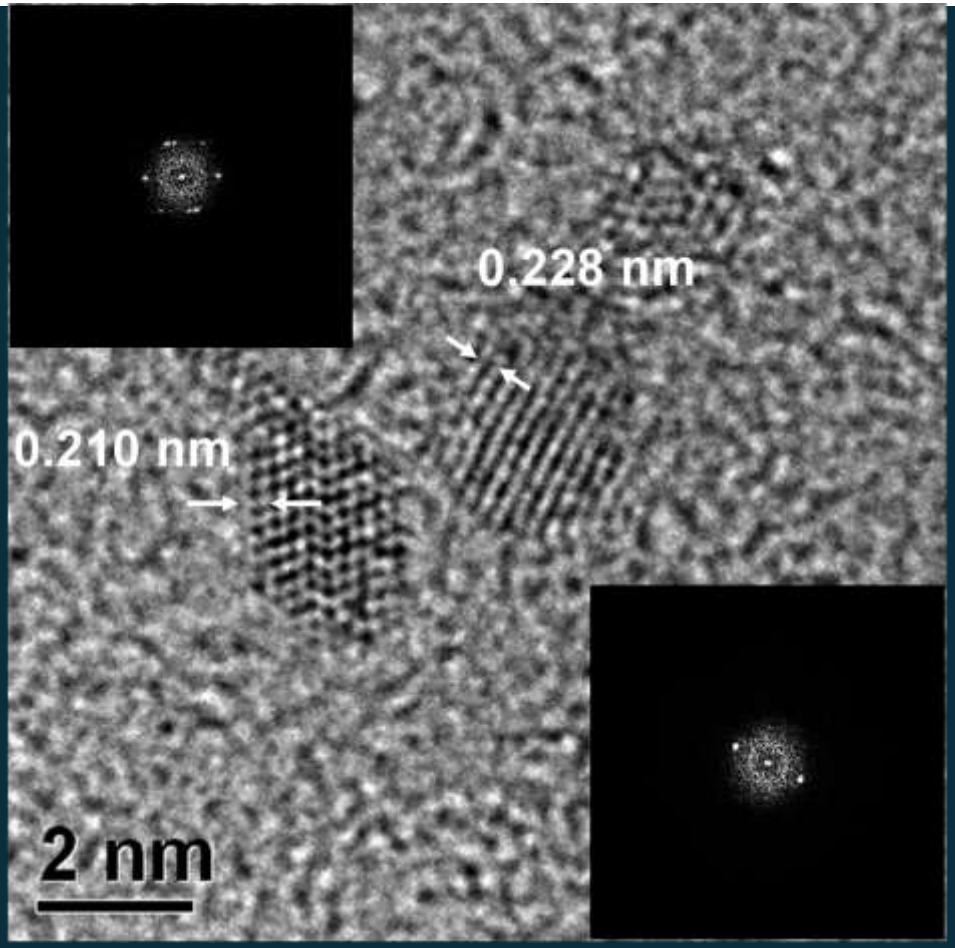

5 nm



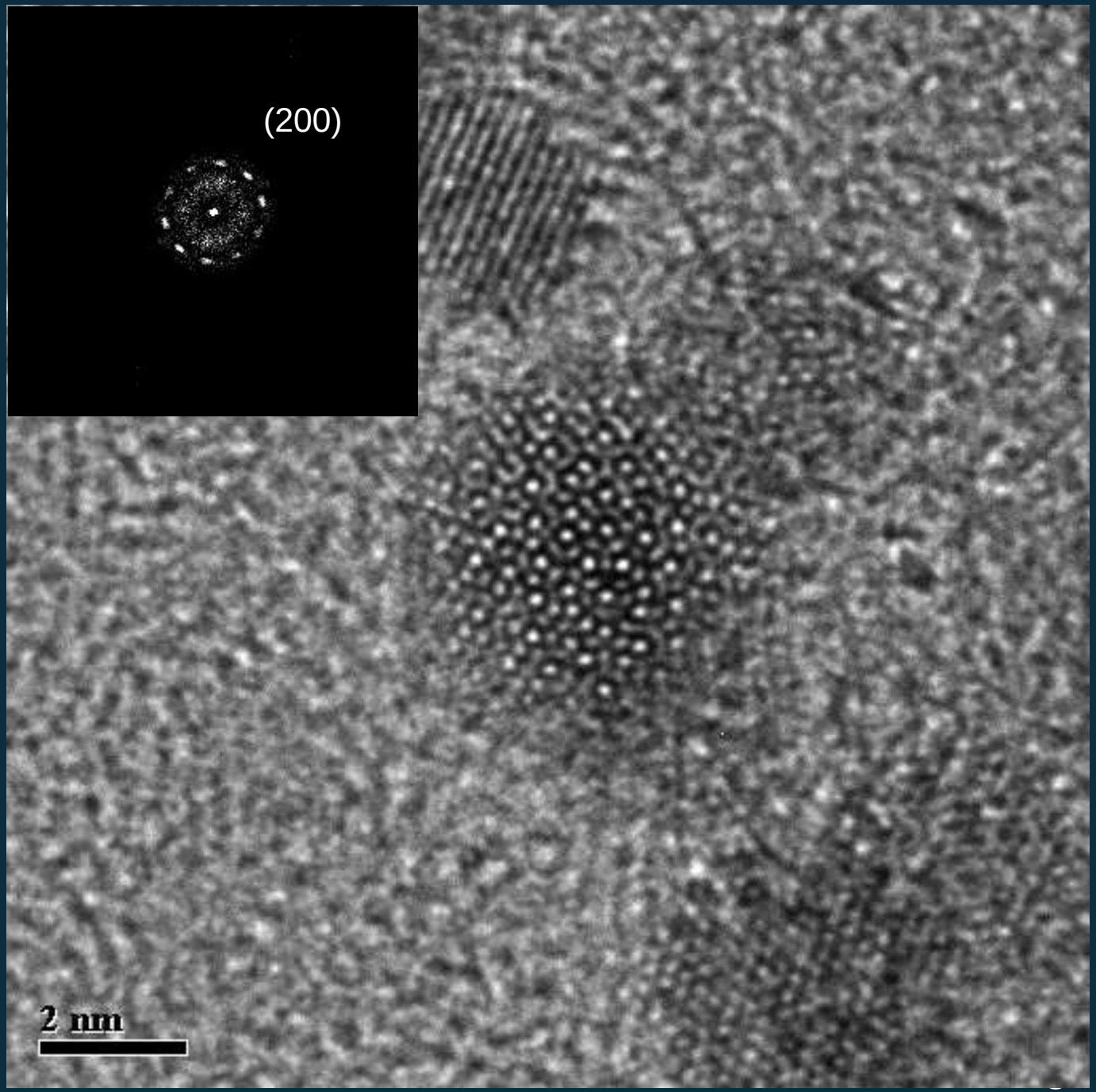



2 nm



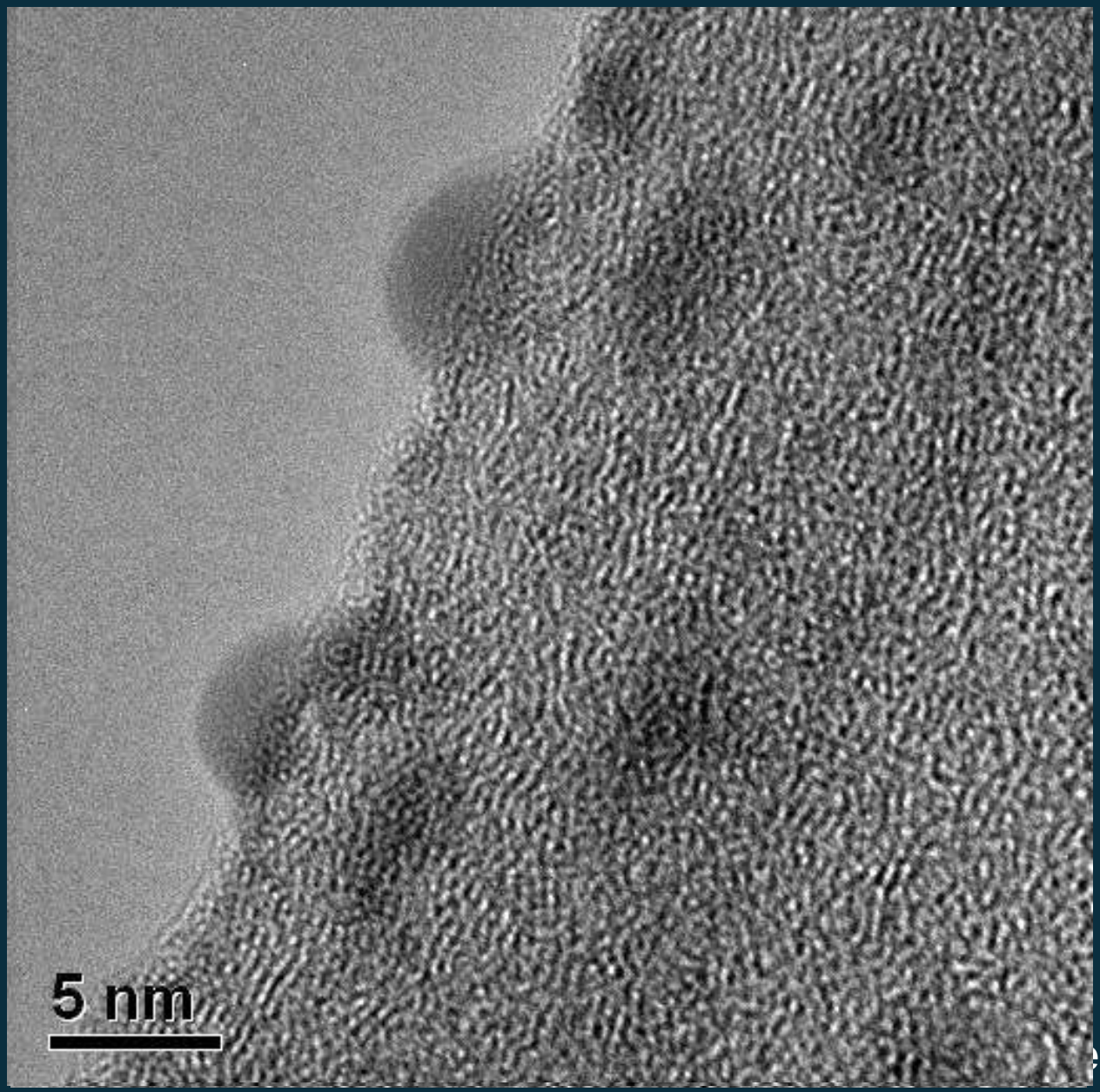




Bimetalic Nanoparticles of RuPt


(200)
2 nm

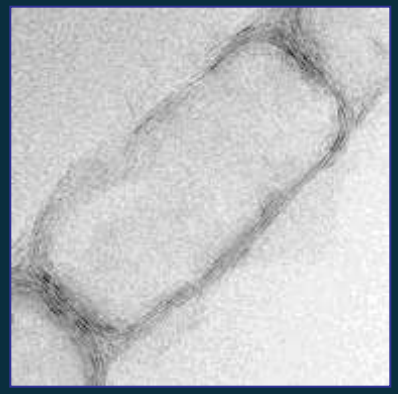
# Bismuth nanoparticles

Spontaneous rotations of bismuth nanoparticles

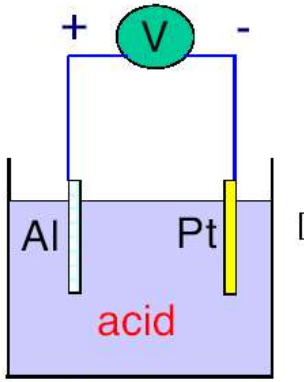


# Síntesis y estudio de Sistemas Unidimensionales

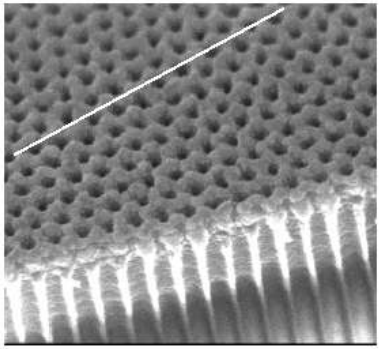
# $MoS_2$ NANOTUBES



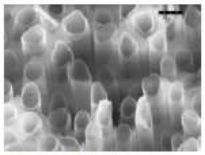
# Nanoporous $Al_2O_3$ templates



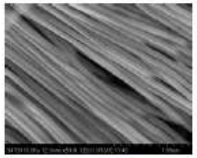

electrochemical self-assembly



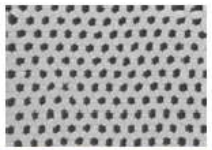

anodic aluminum oxide (AA0) templates



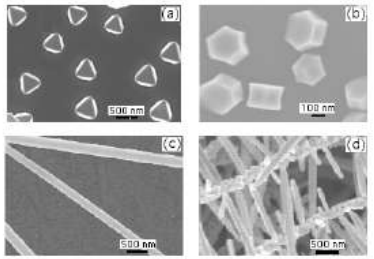
nanotubes



nanowires



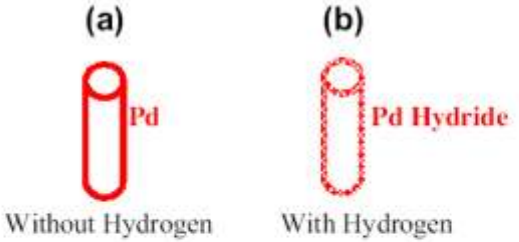
nano networks



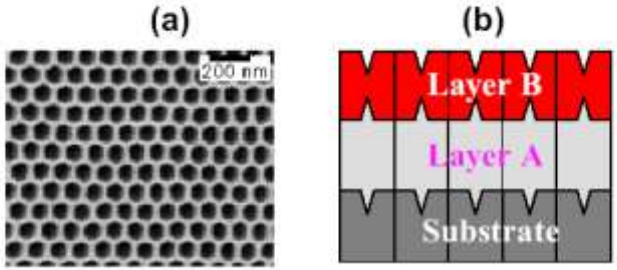

high-speed electrodeposition nanocrystals for
*physical confinement*
*chemical catalysis*
*surface functionalization*

# Palladium Based Hydrogen Nanosensors

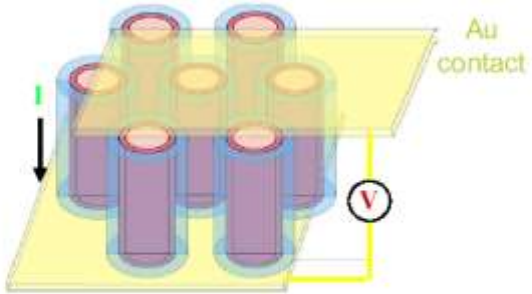
## Nanotube Sensors




**Operating Mechanism:** Resistance changes due to the formation of palladium hydride in the presence of hydrogen



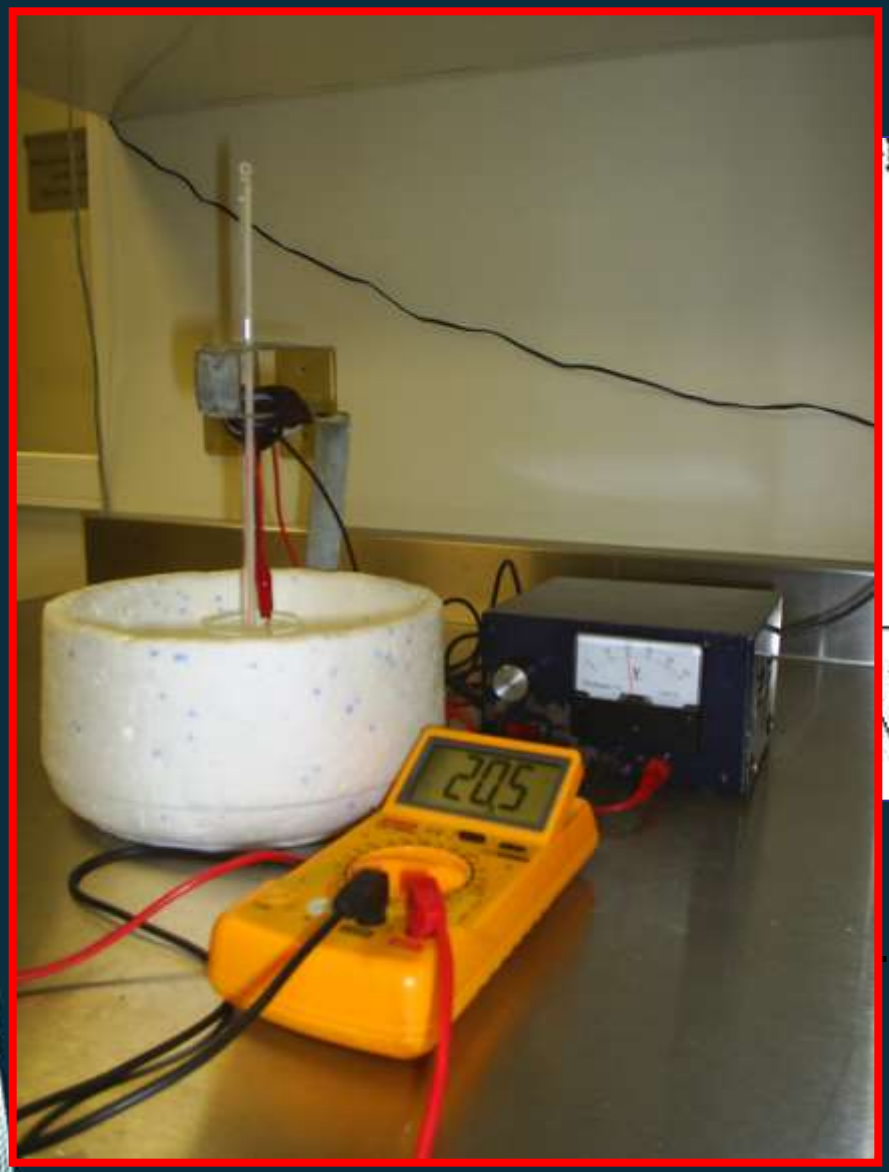

**Nanotube Fabrication:** Atomic layer deposition (ALD) method will be used to deposit palladium on the walls of nanopores in anodic aluminum oxide (AAO) membrane (a) Nanopore arrays in AAO membrane, (b) Schematic illustration for atomic layer deposition (ALD) process.

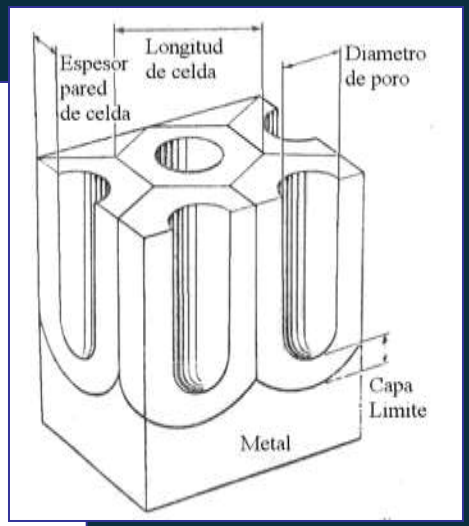



**Equivalent Circuits** of the sensors

Short diffusion distance: High speed
Large number of nanotubes: High signal/noise ratio

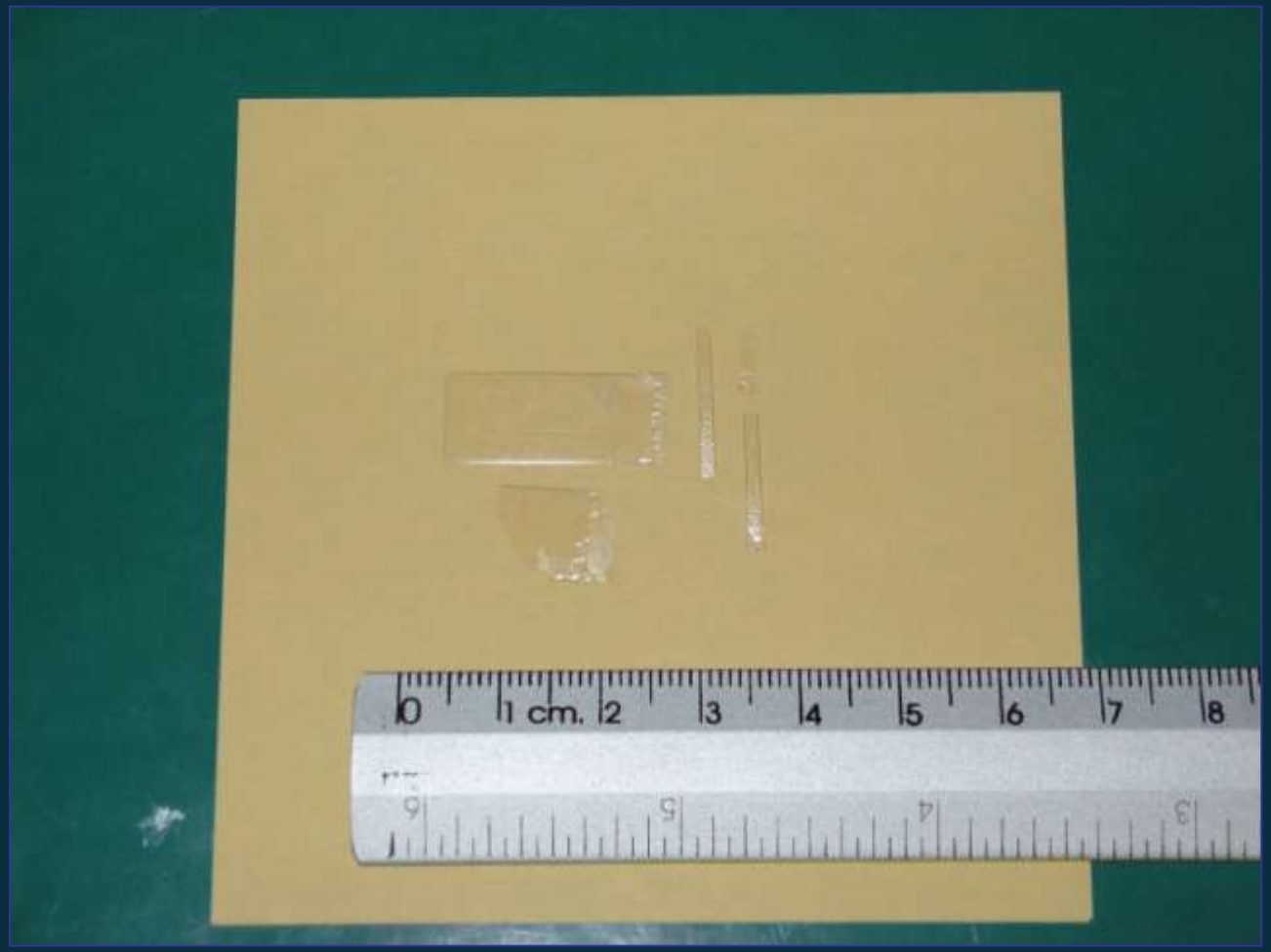
# ALUMINA TEMPLATES



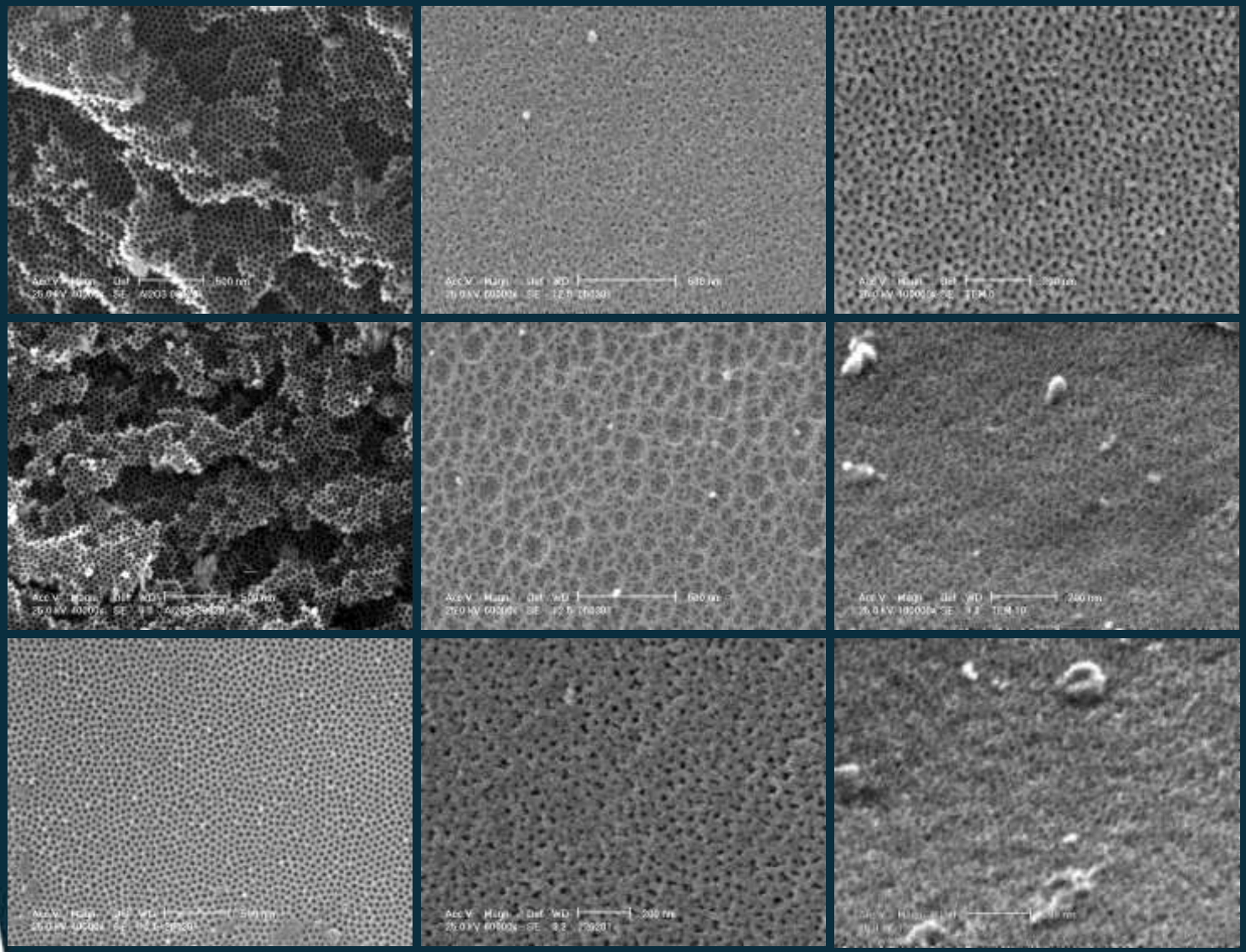




$+ 3H_2\uparrow + 3SO_3$

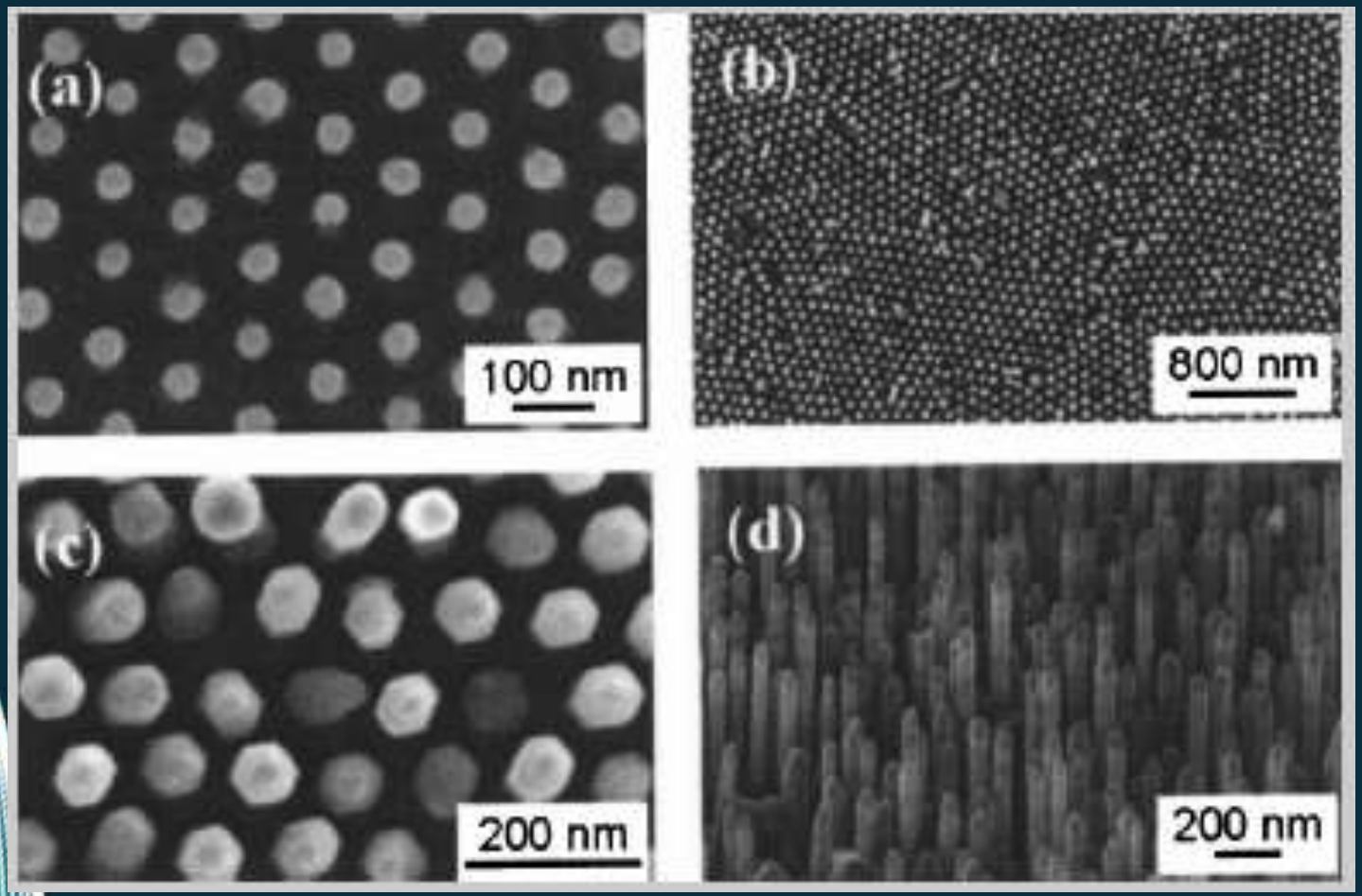
# ALUMINA TEMPLATES



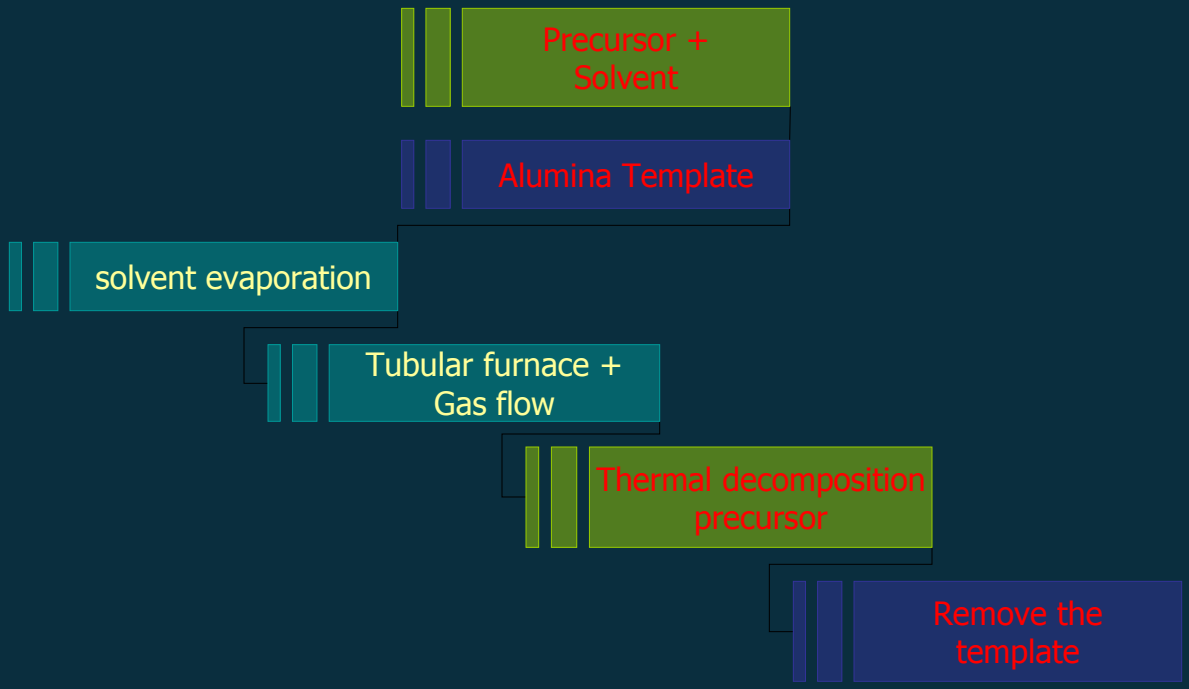
# $Al_2O_3$ TEMPLATES SEM



# $Al_2O_3$



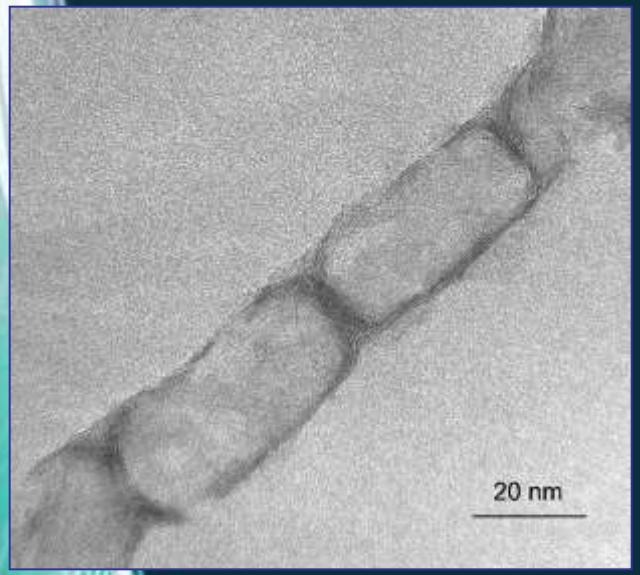
# DESCOMPOSICIÓN TÉRMICA



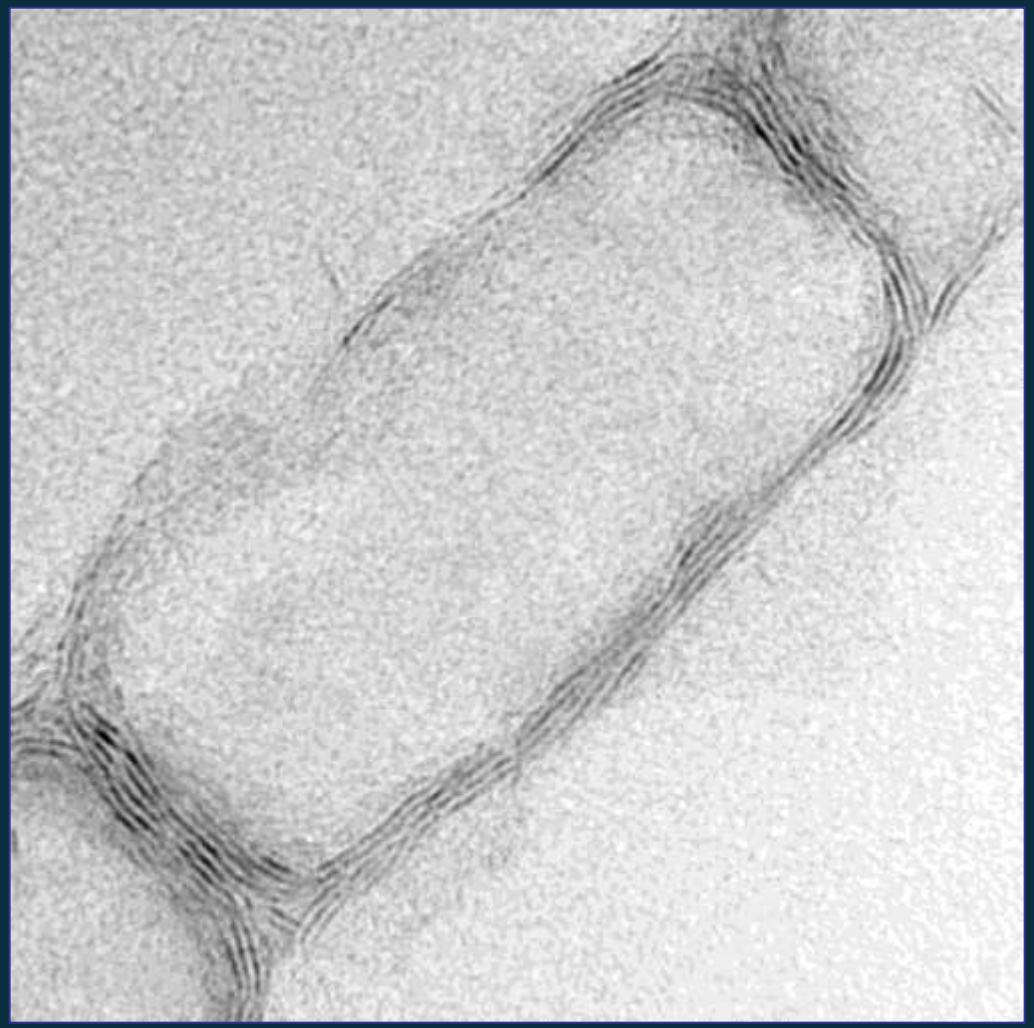
# FURNACE SYSTEM

# Before thermal treatment

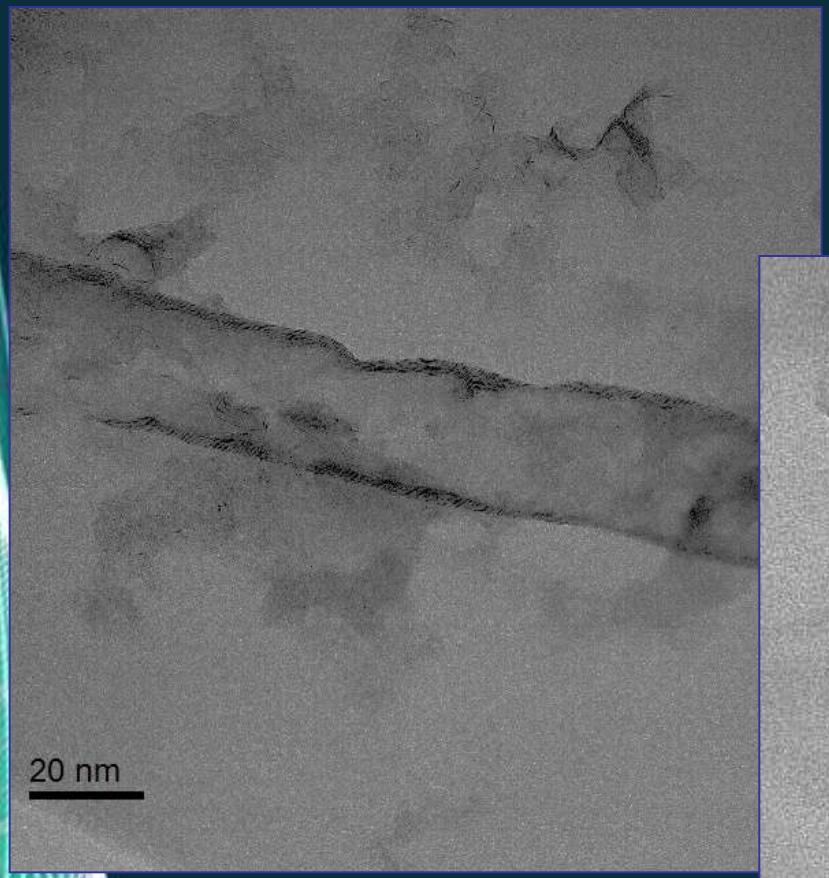
# $MoS_2$ NANOTUBES

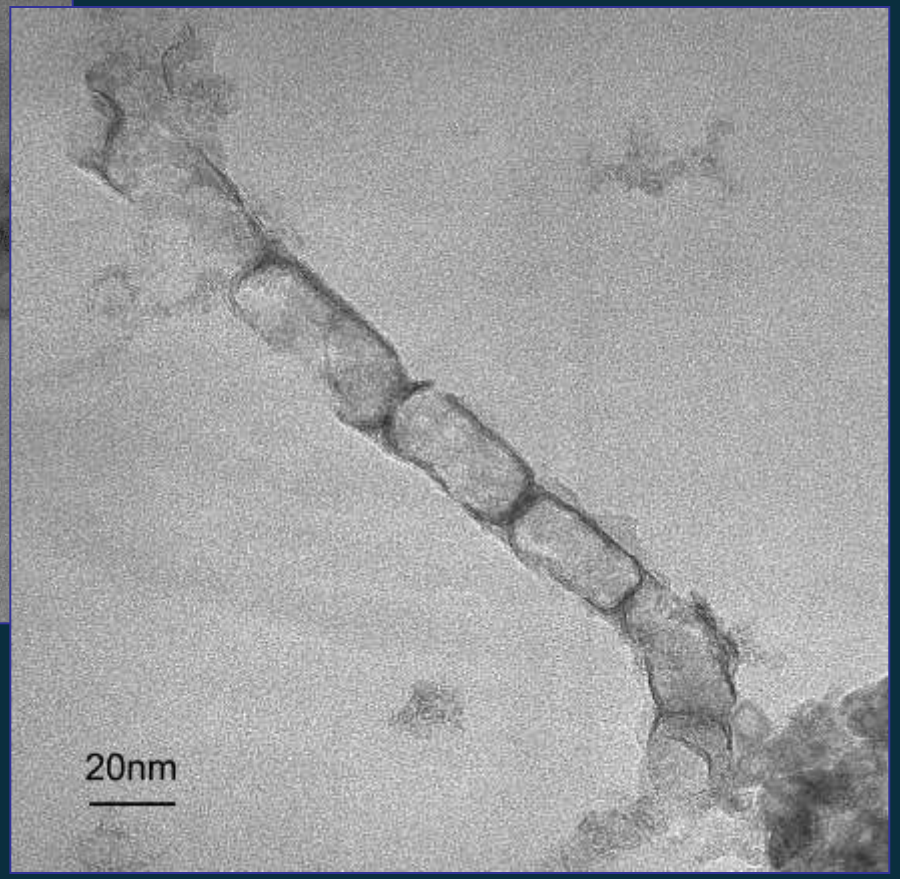



PRECURSOR Ammonium Tetratiomolybdate

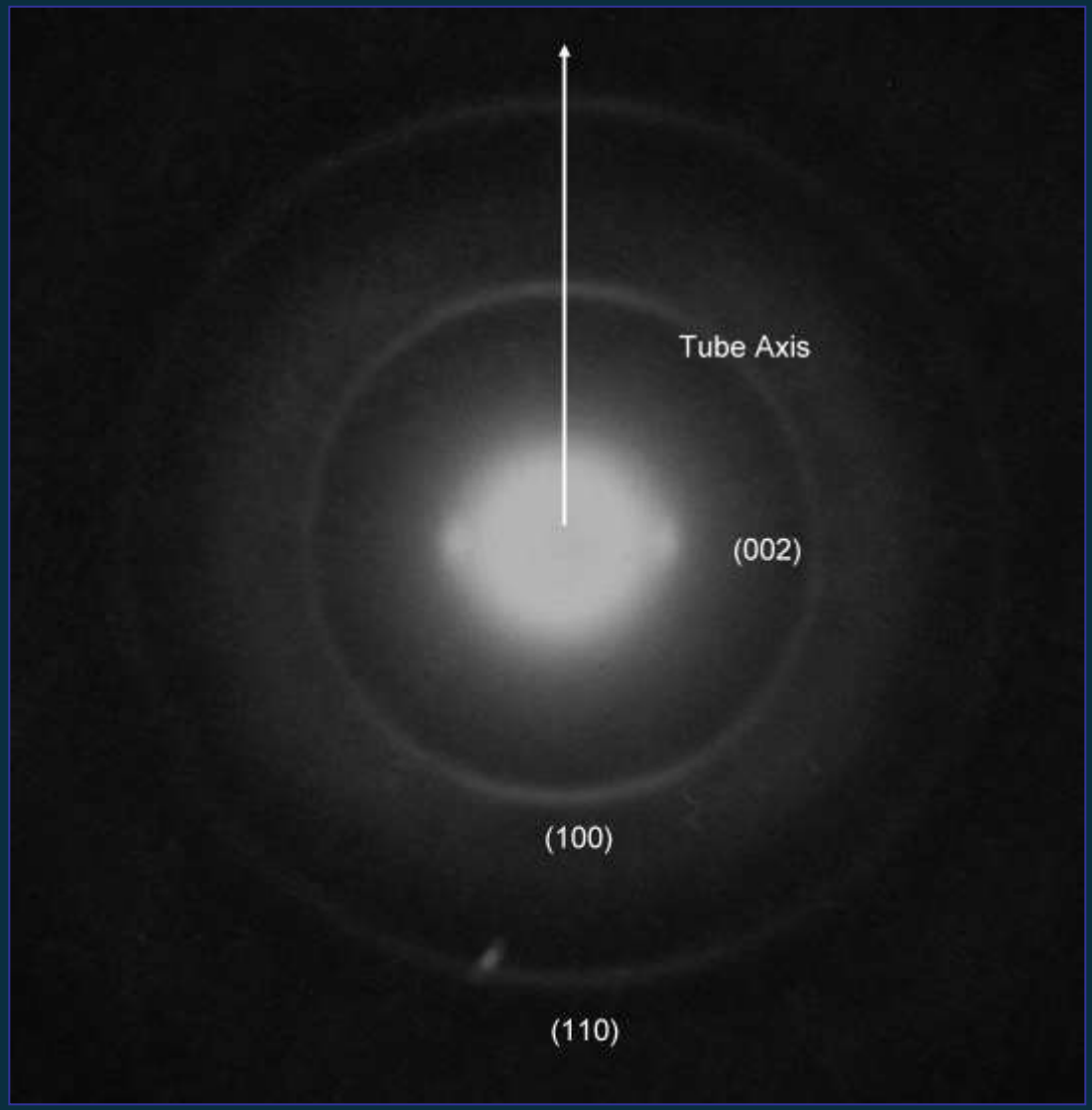


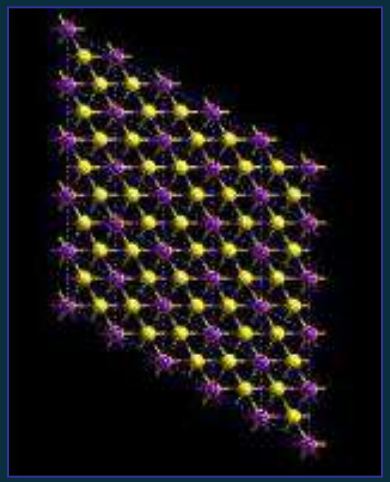
# $MoS_2$ NANOTUBES MORPHOLOGY

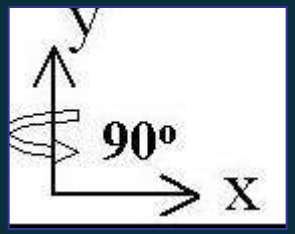


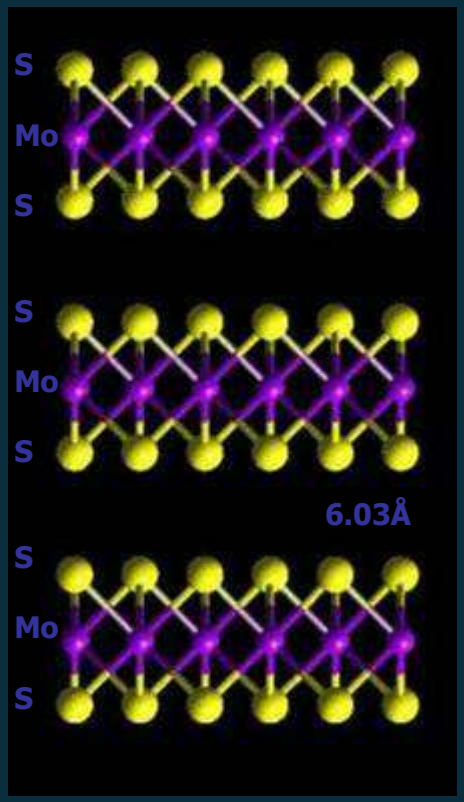



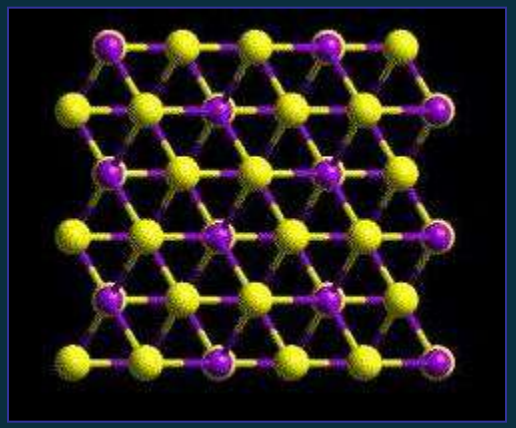
# ELECTRON DIFFRACTION PATTERN





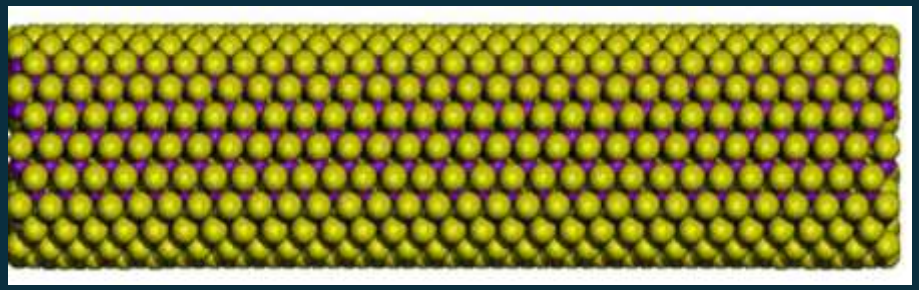

y
90°
x

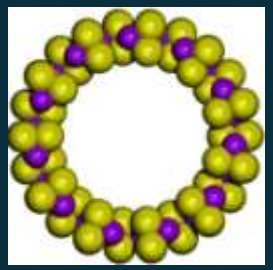

S
Mo
S
S
Mo
S
6.03Å
S
Mo
S



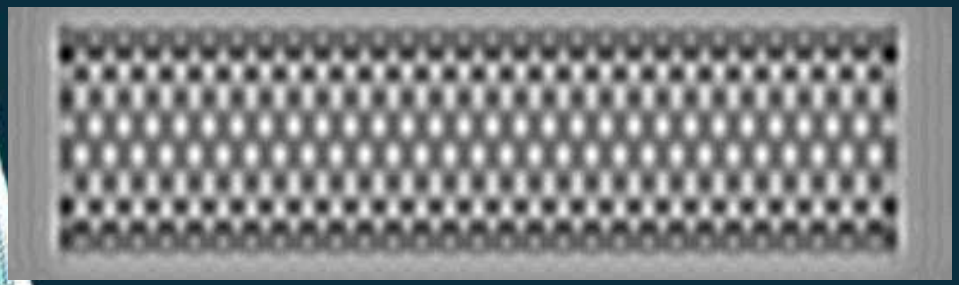
# $MoS_2$ SIMULATION

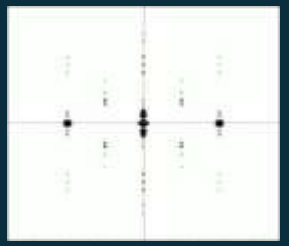
nanotube(671,1342) wide: 22, lenght:28



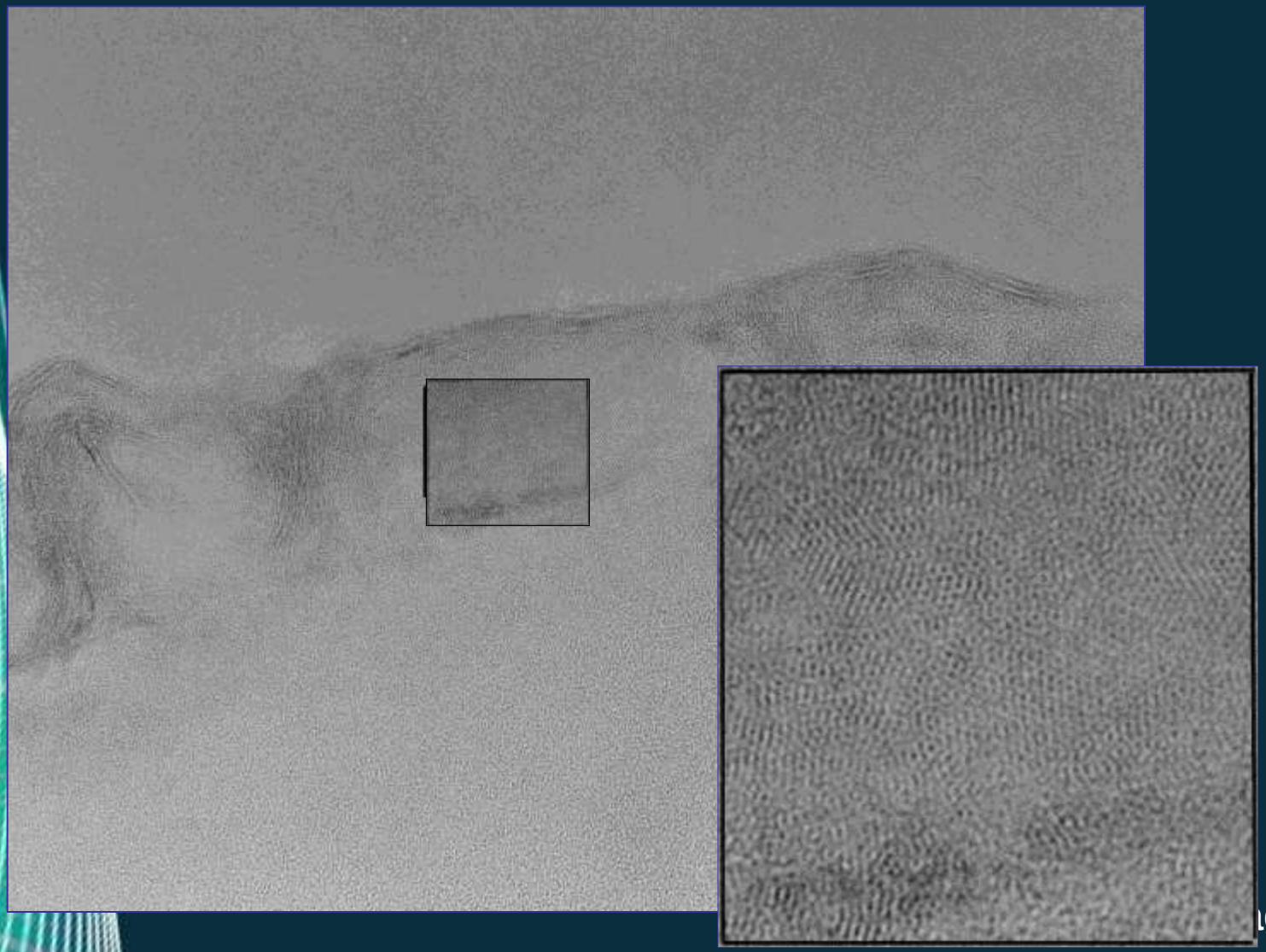


**Energy:**
-139535 Kev



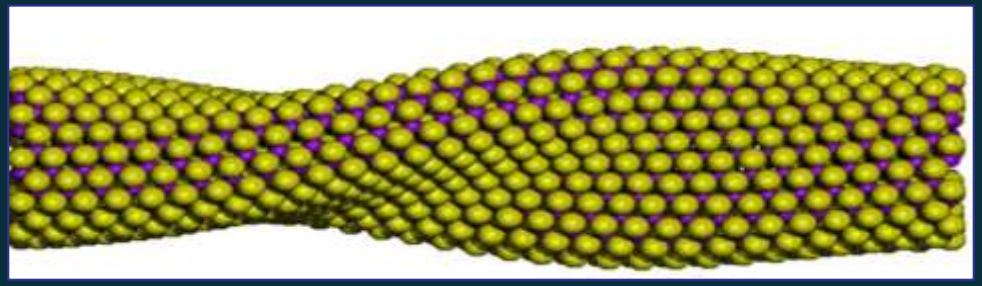


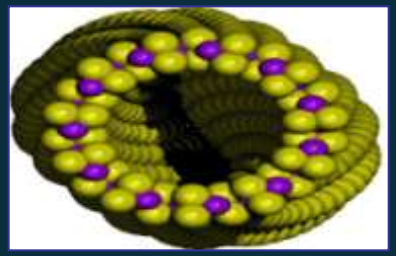
# $MoS_2$ TWISTED NANOTUBES



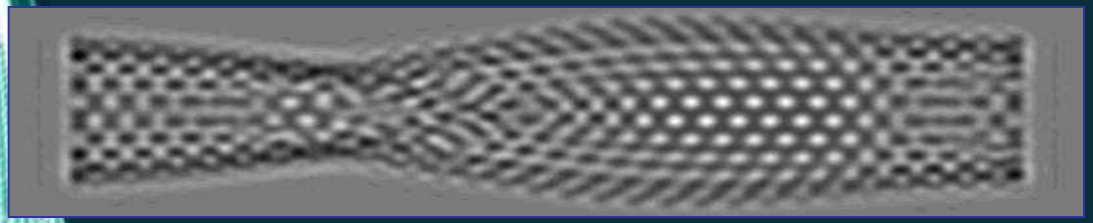
# $MoS_2$ SIMULATION

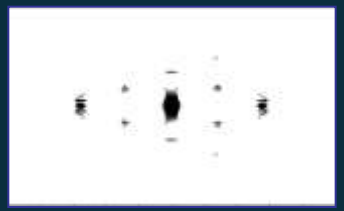
Stable model, torsion effect is present.



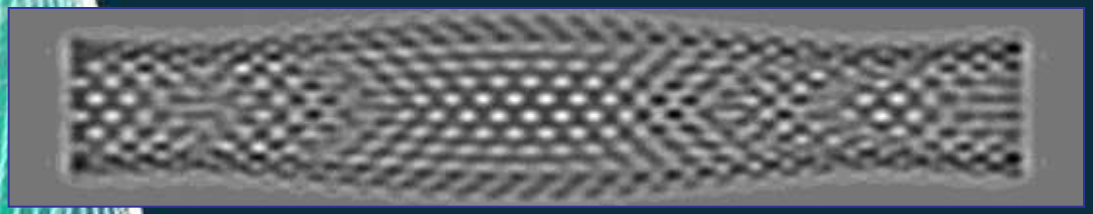


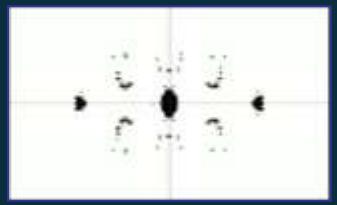
**Energy:**
-144613 Kev



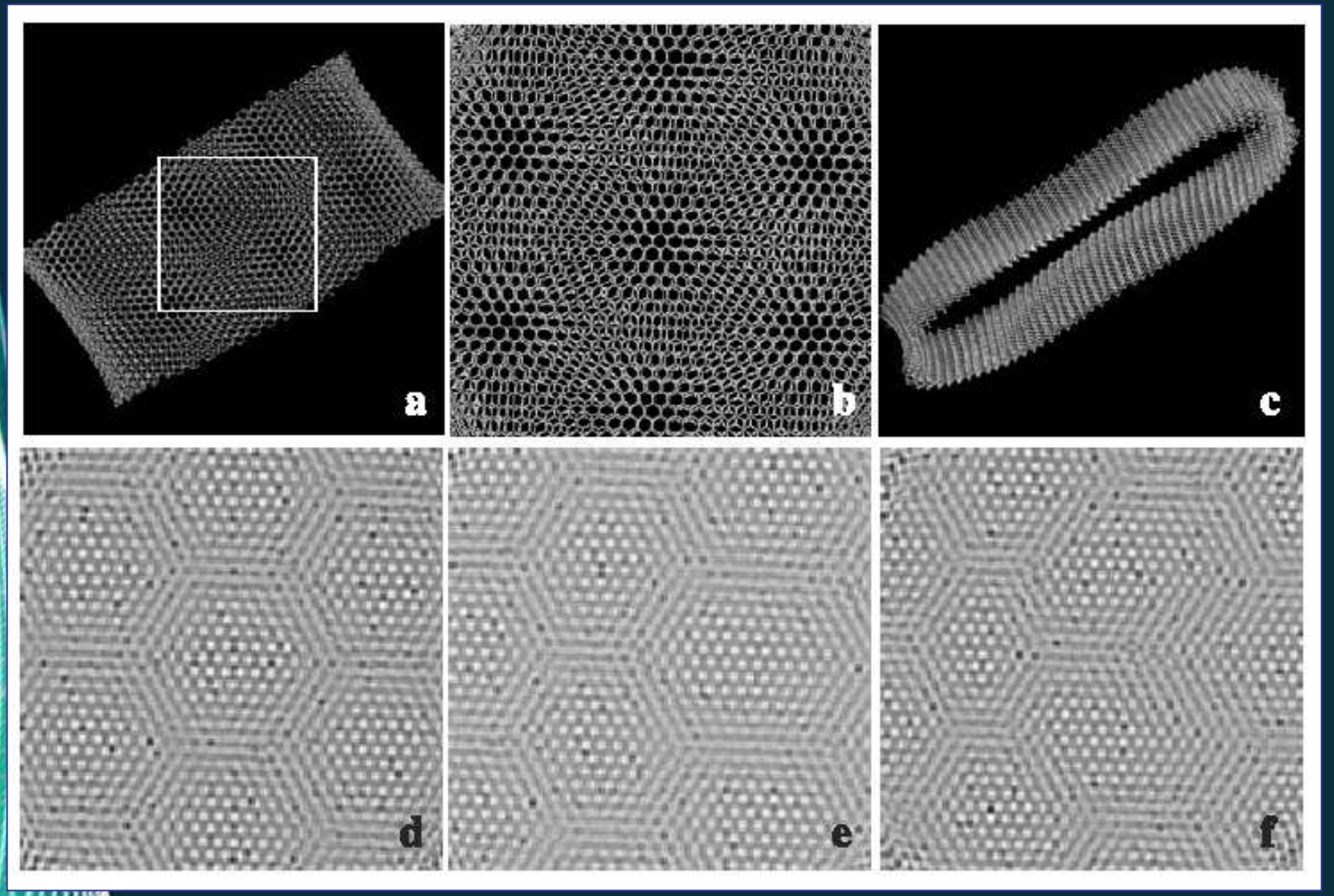


Another view of the same model.

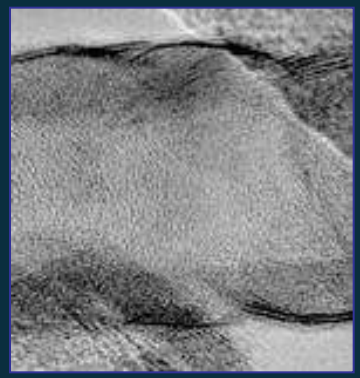




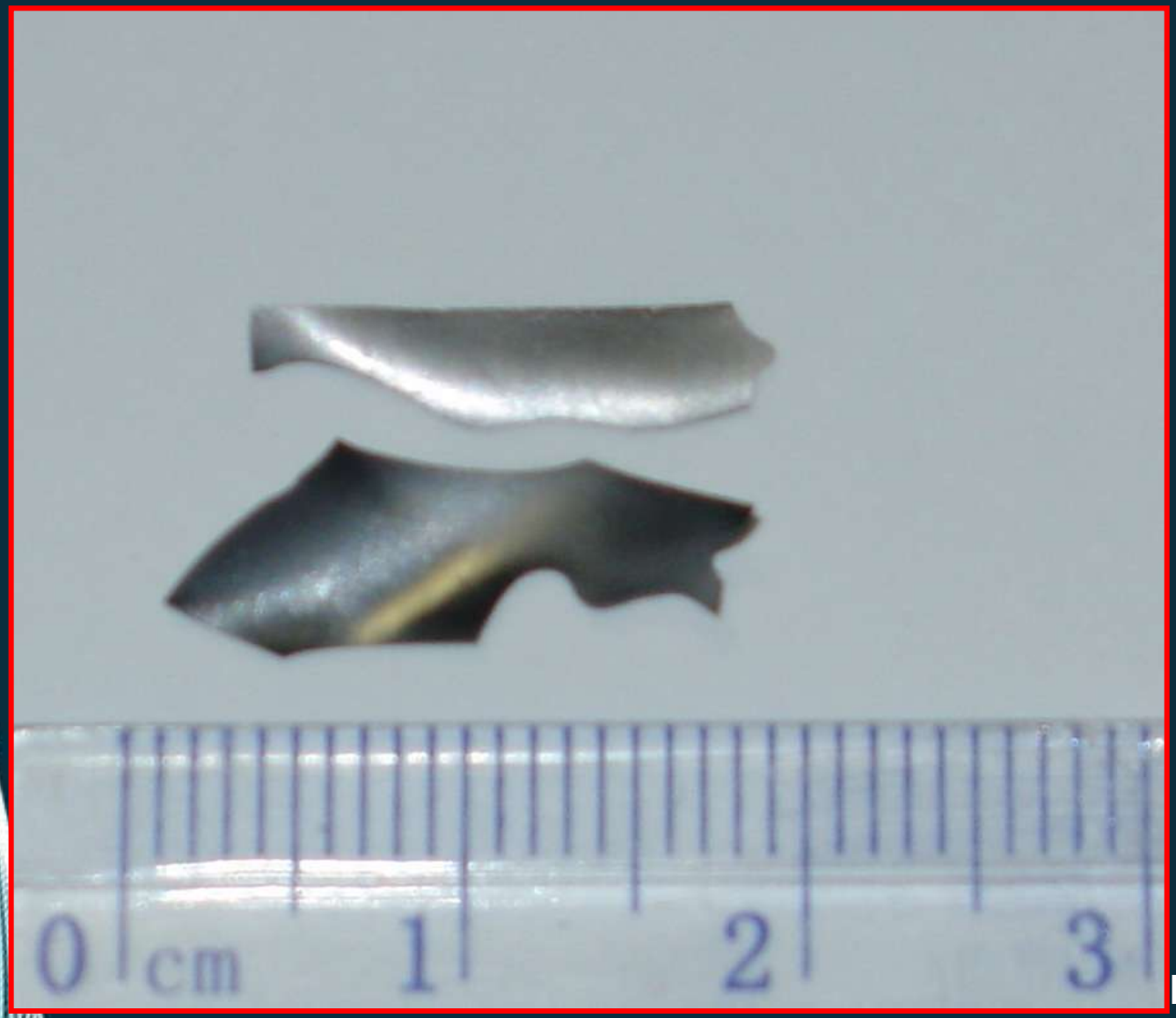
# MOIRÉ's DOMAINS



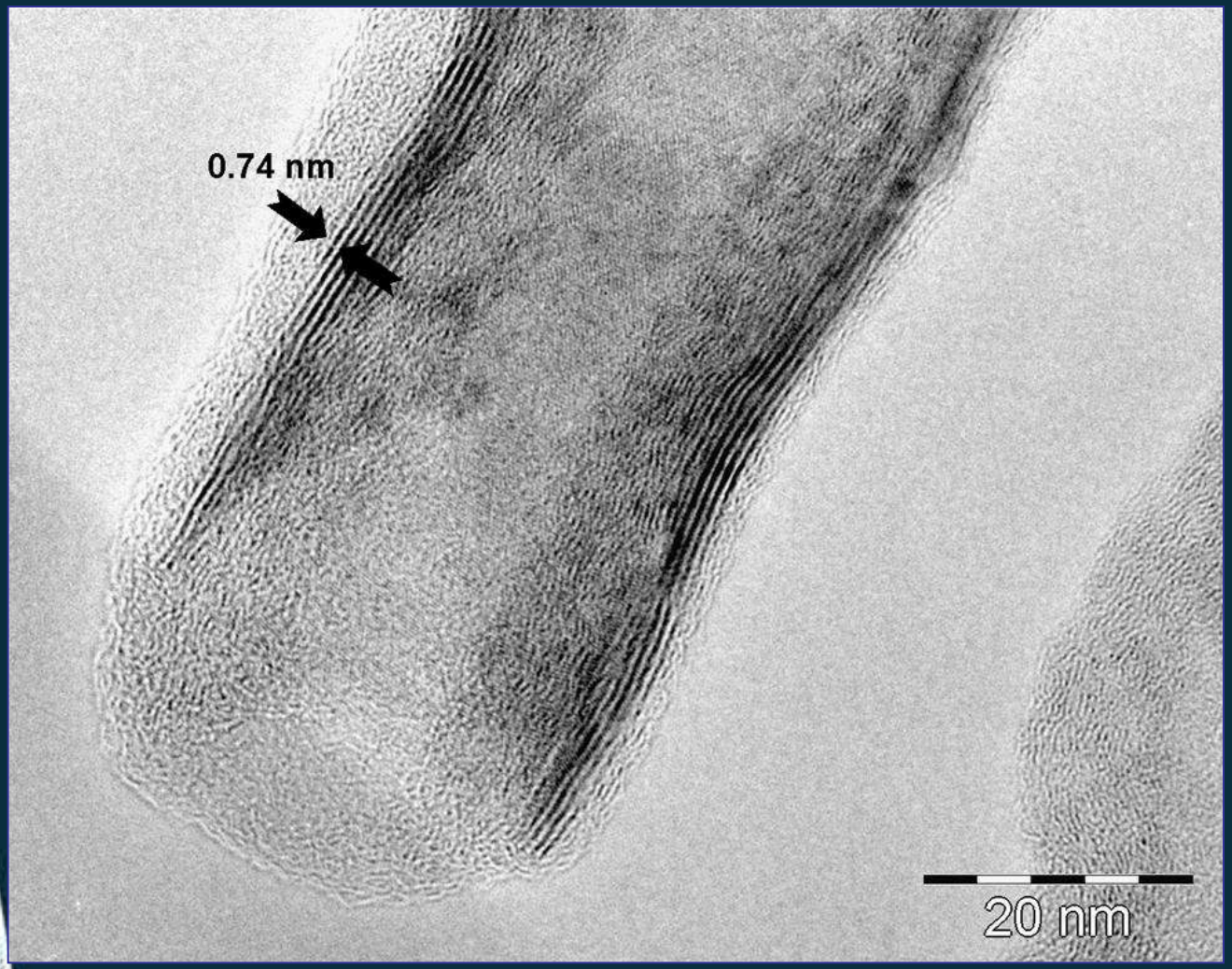
# COAXIAL $MoS_2$ + C NANOTUBES



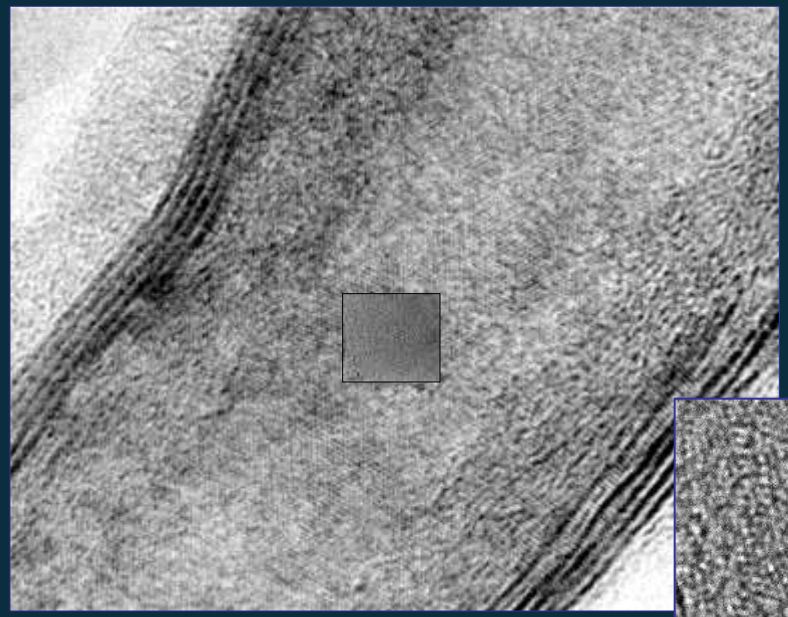
# AFTER THERMAL TREATMENT

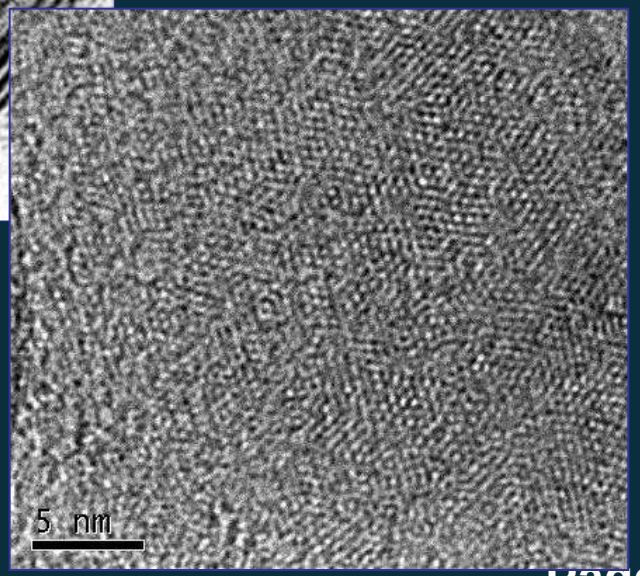


# $MoS_2$ + C NANOTUBES



# $MoS_2$ + C NANOTUBES






PRECURSORS
1. AMMONIUM TETRATIOMOLYBDATE
2. PROPYLENE GAS

# Nanotubos coaxiales

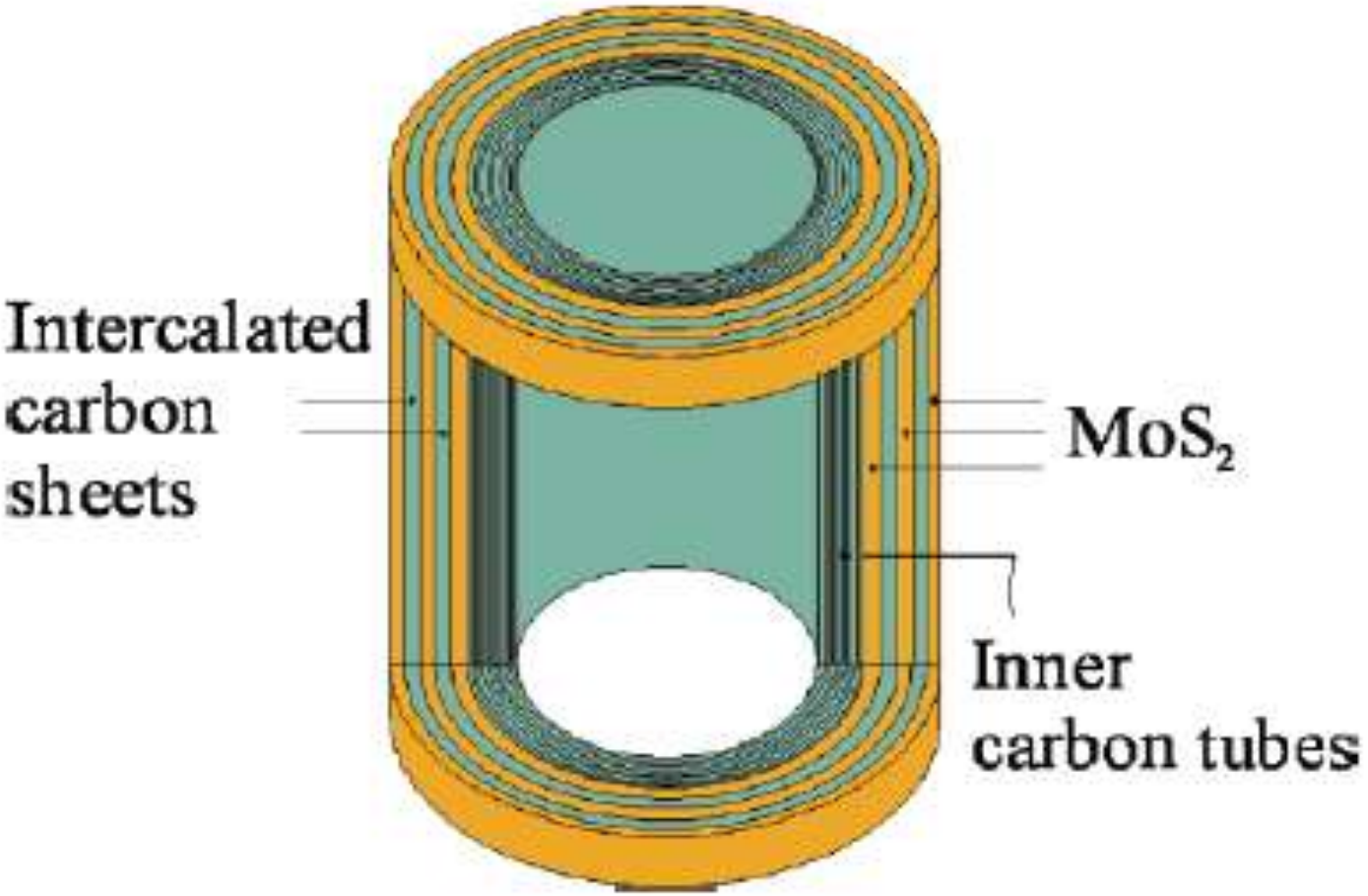
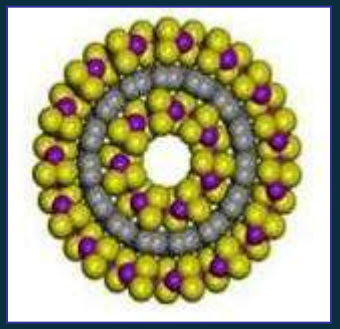
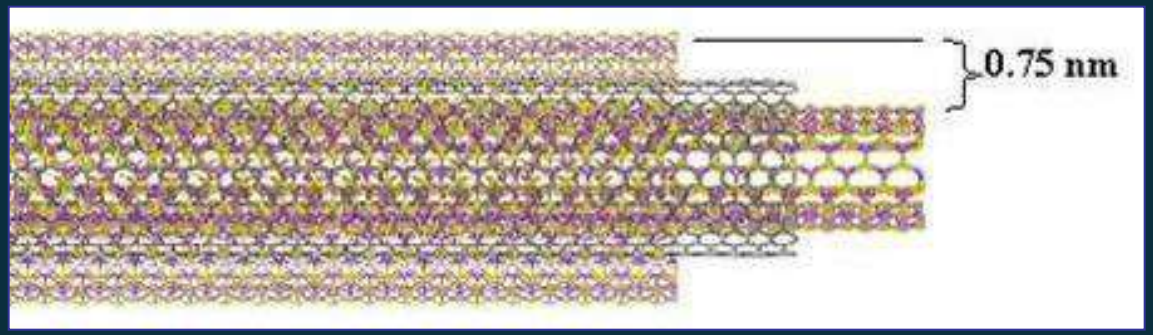


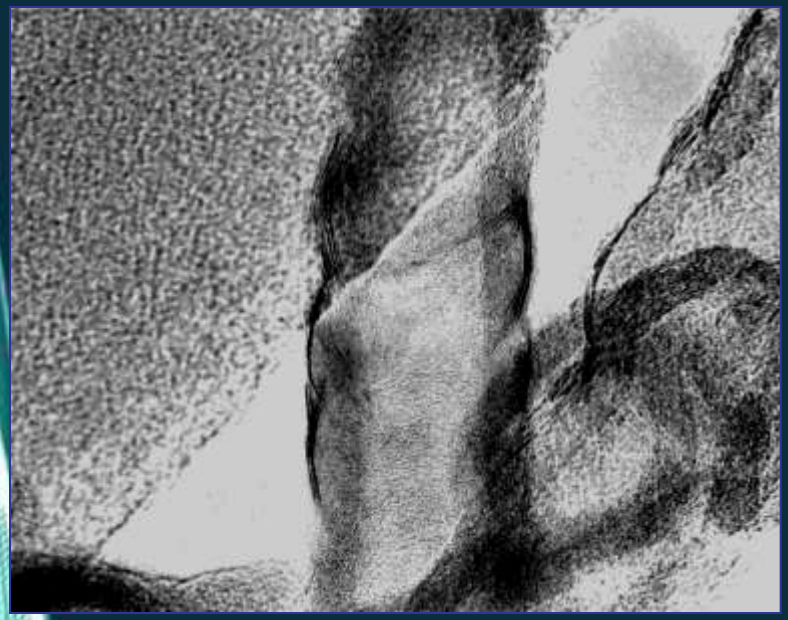

**Figure 2.** Schematic diagram of a coaxial intercalated $MoS_2$–C nanotube with a pure graphite phase inside.

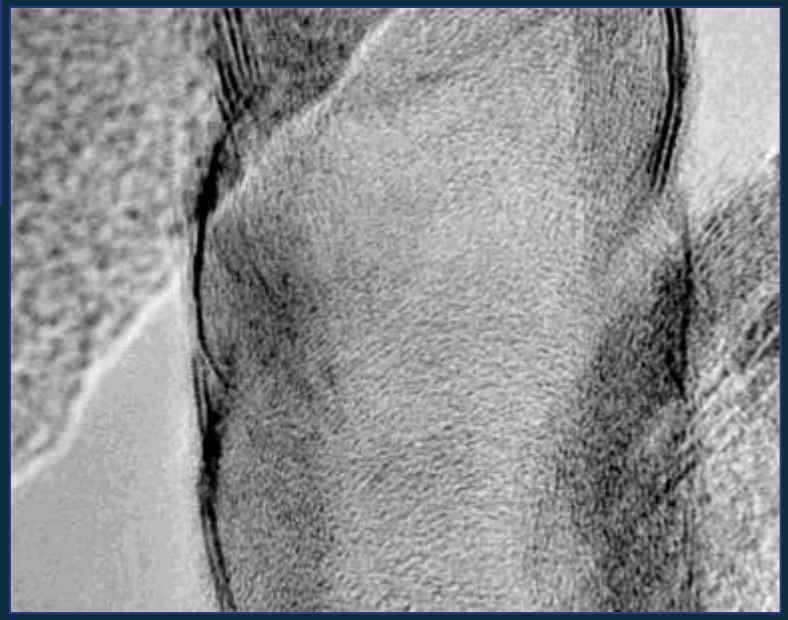
# $MoS_2$ + C SIMULATION



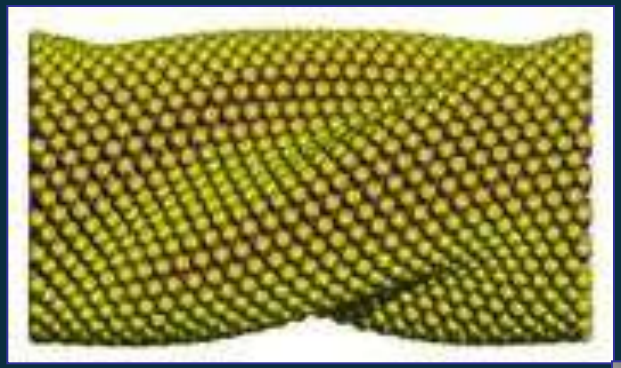


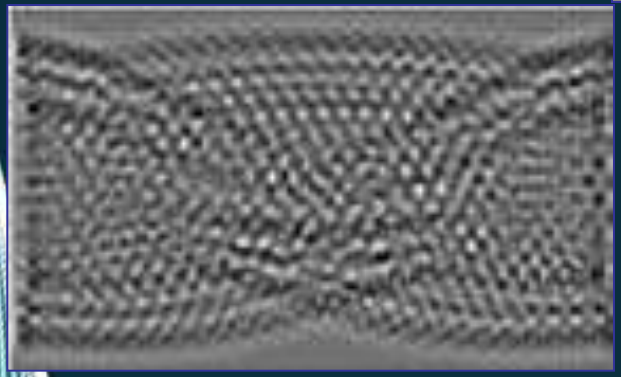
# $MoS_2$ + C NANOTUBES

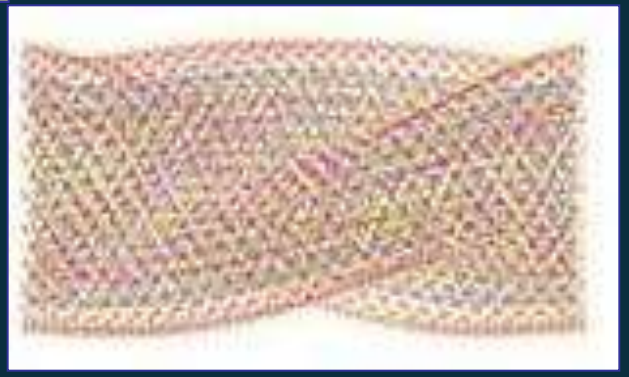




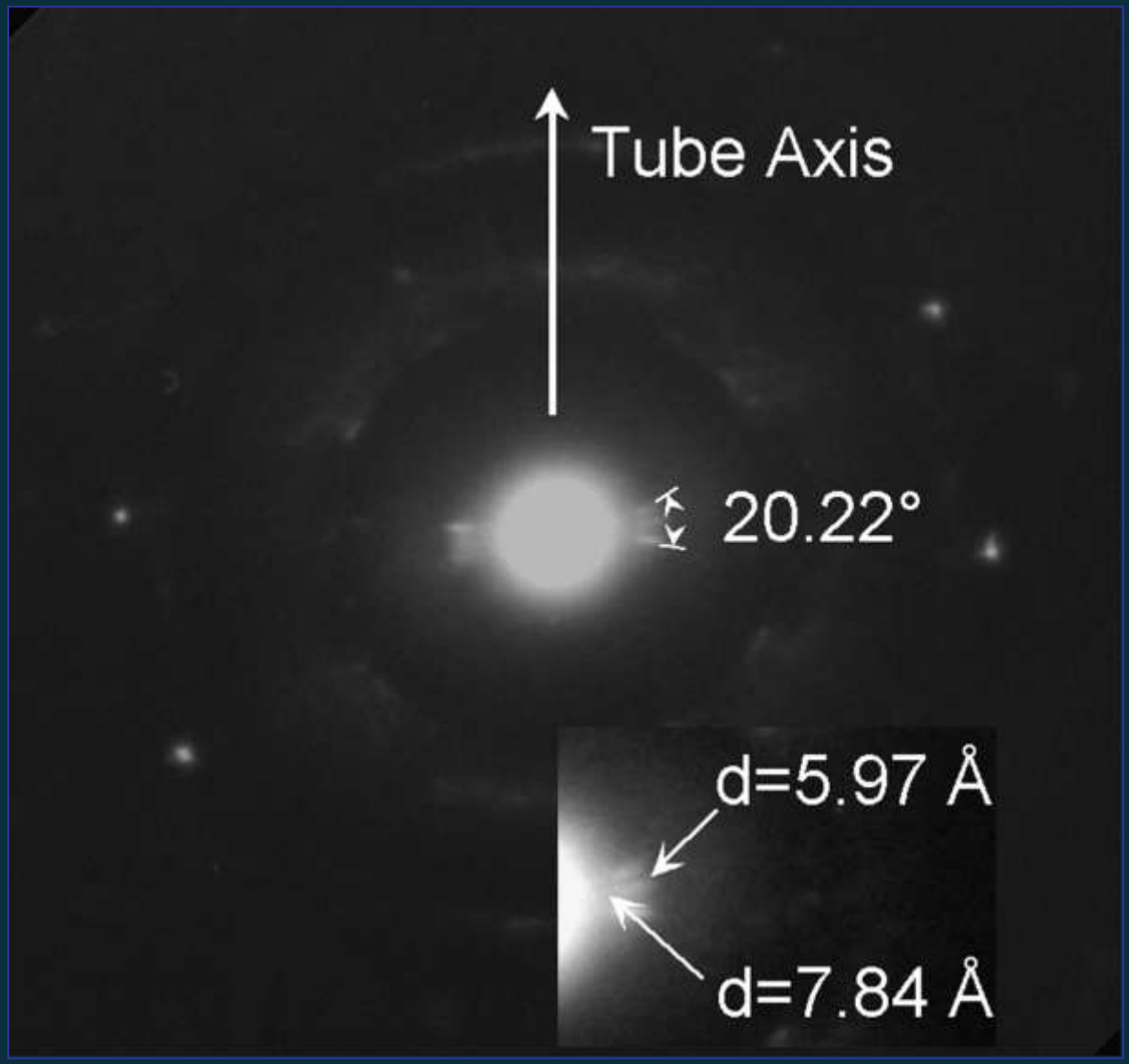
# $MoS_2$ + C SIMULATION





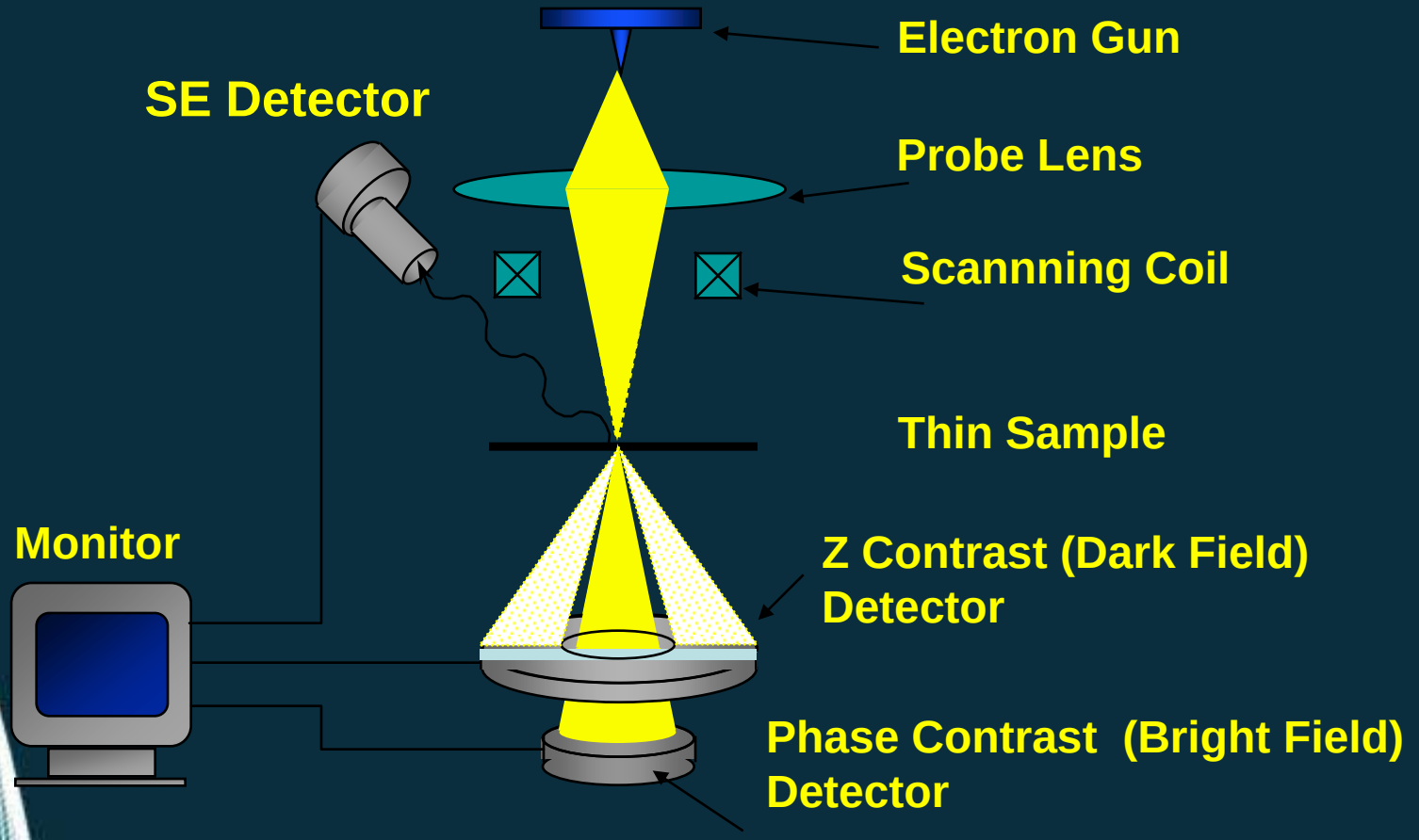


# ELECTRON DIFFRACTION PATTERN

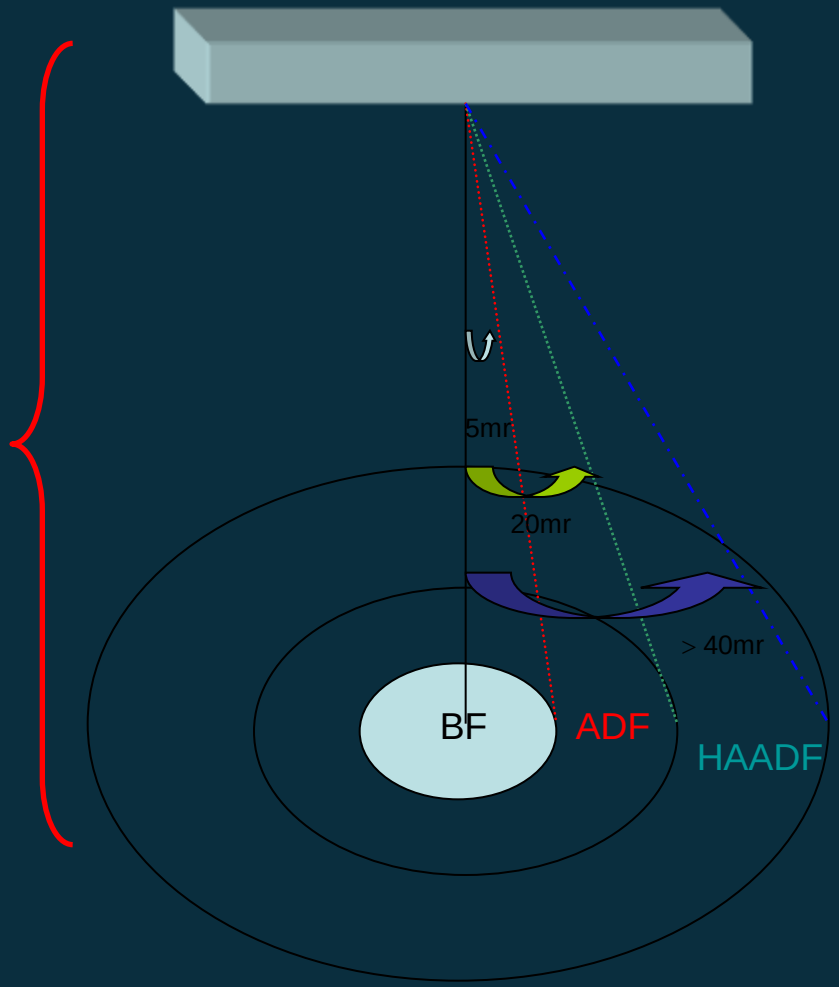


# Incoherence atomic high resolution scanning transmission electron microscopy images

# STEM : HAADF


Electron Gun
SE Detector
Probe Lens
Scannning Coil
Thin Sample
Monitor
Z Contrast (Dark Field) Detector
Phase Contrast (Bright Field) Detector

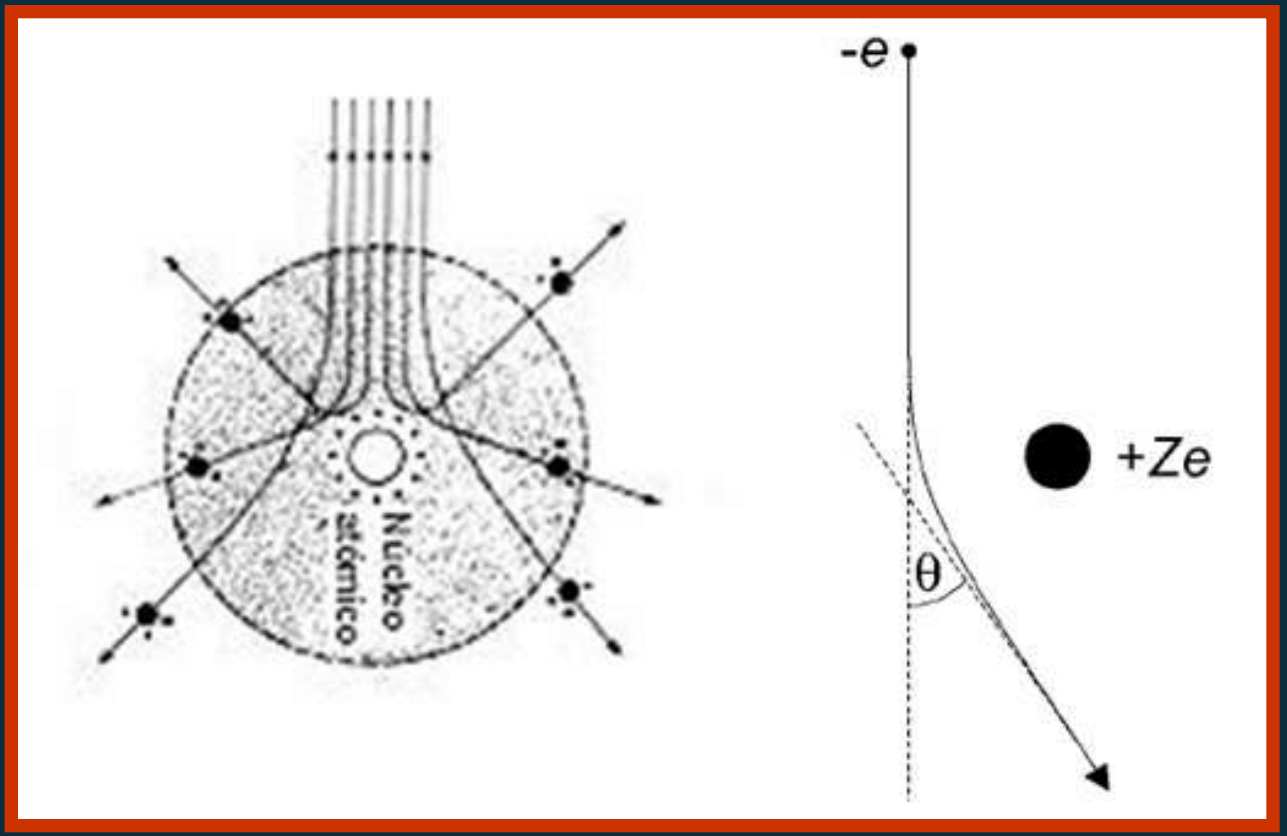
12 cm = L



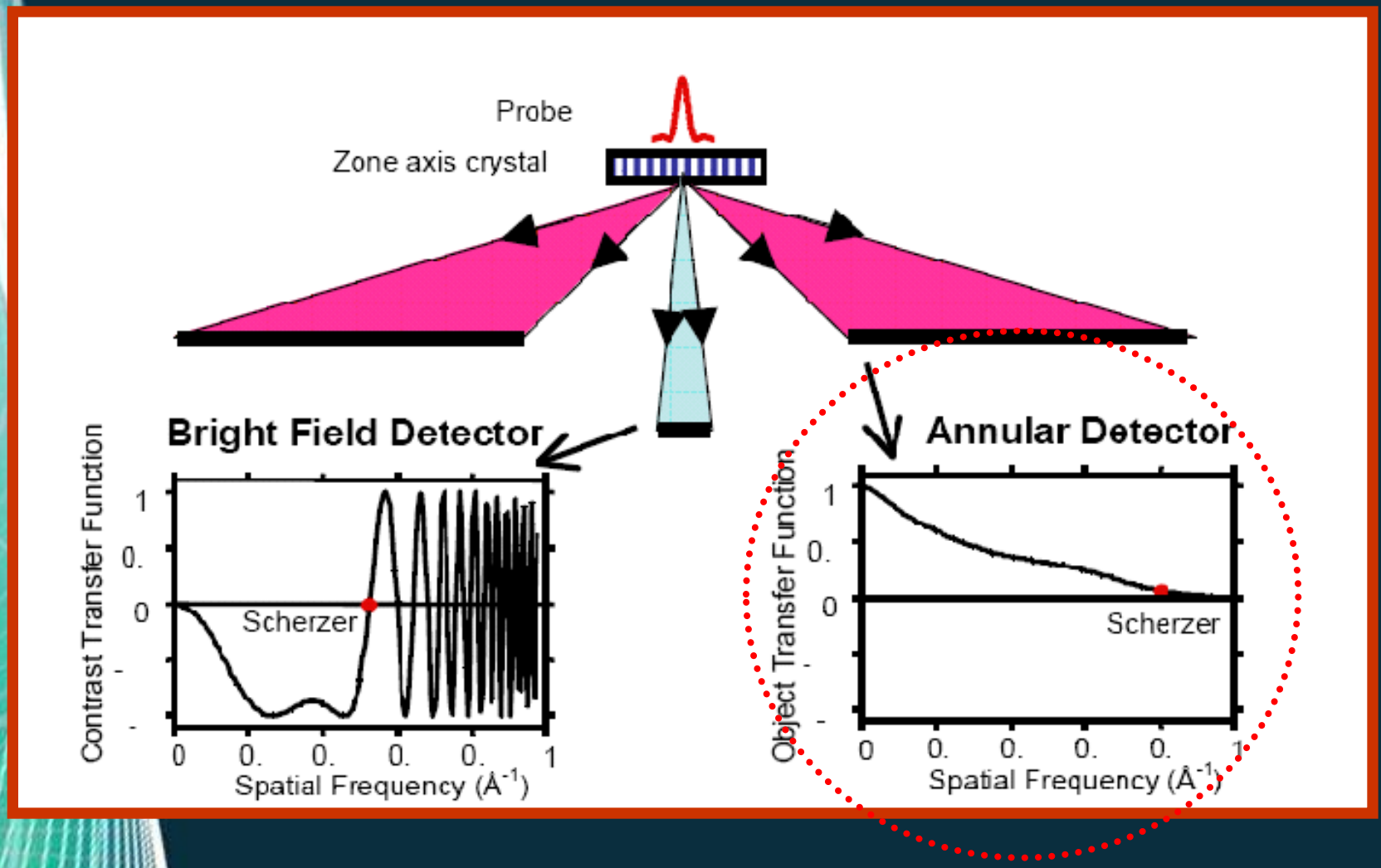

Three different detectors

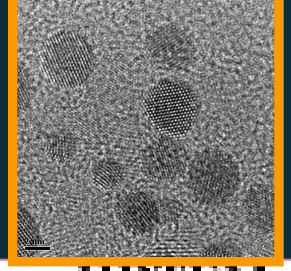
- BF
- ADF
- HAADF
- Low Camera length L

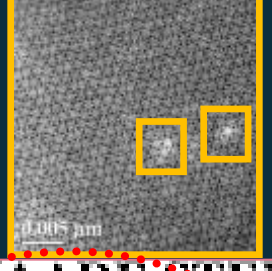
## RUTHERFORD SCATTERING

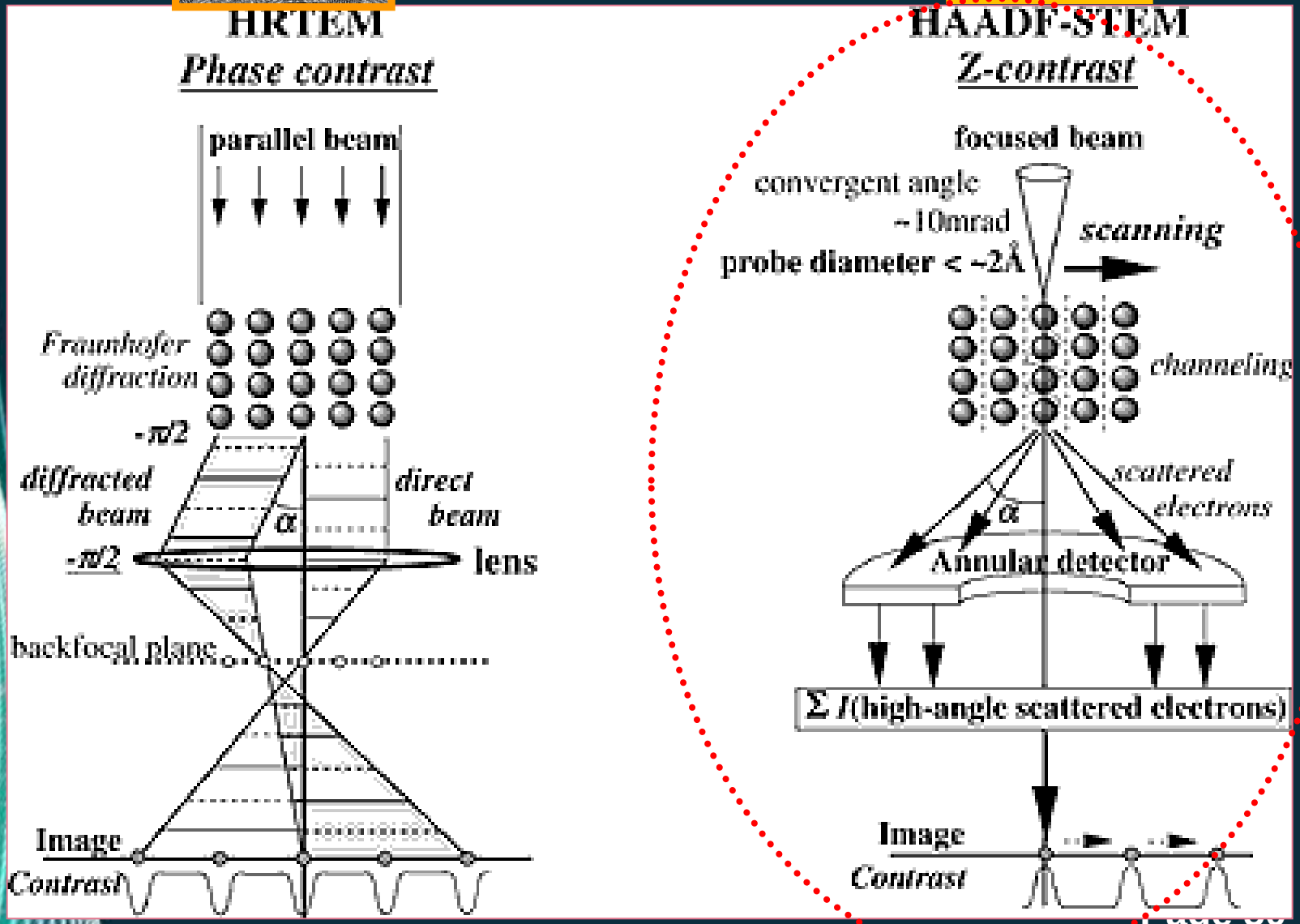



$$\mathbf{G = k\, Z_j^{\alpha} = \delta I}$$


Probe
Zone axis crystal
Bright Field Detector
Annular Detector
Contrast Transfer Function
Object Transfer Function
Scherzer
Scherzer
Spatial Frequency (Å-1)
Spatial Frequency (Å-1)

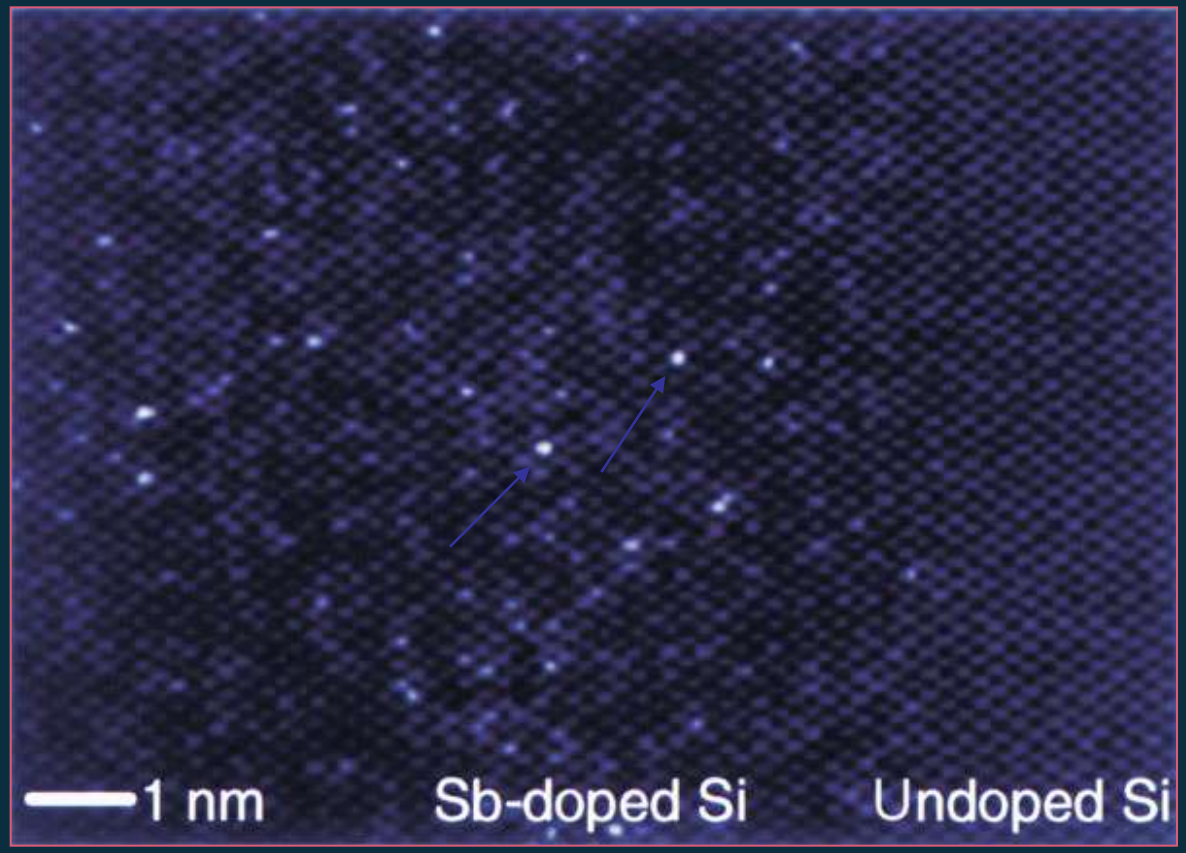





HRTEM
Phase contrast
parallel beam
Fraunhofer diffraction
-π/2
diffracted beam
direct beam
α
-π/2
lens
backfocal plane
Image
Contrast
HAADF-STEM
Z-contrast
focused beam
convergent angle
~10mrad
probe diameter < ~2Å
scanning
channeling
scattered electrons
α
Annular detector
Σ I(high-angle scattered electrons)
Image
Contrast

# Dopant Imagin

## *HAADF*

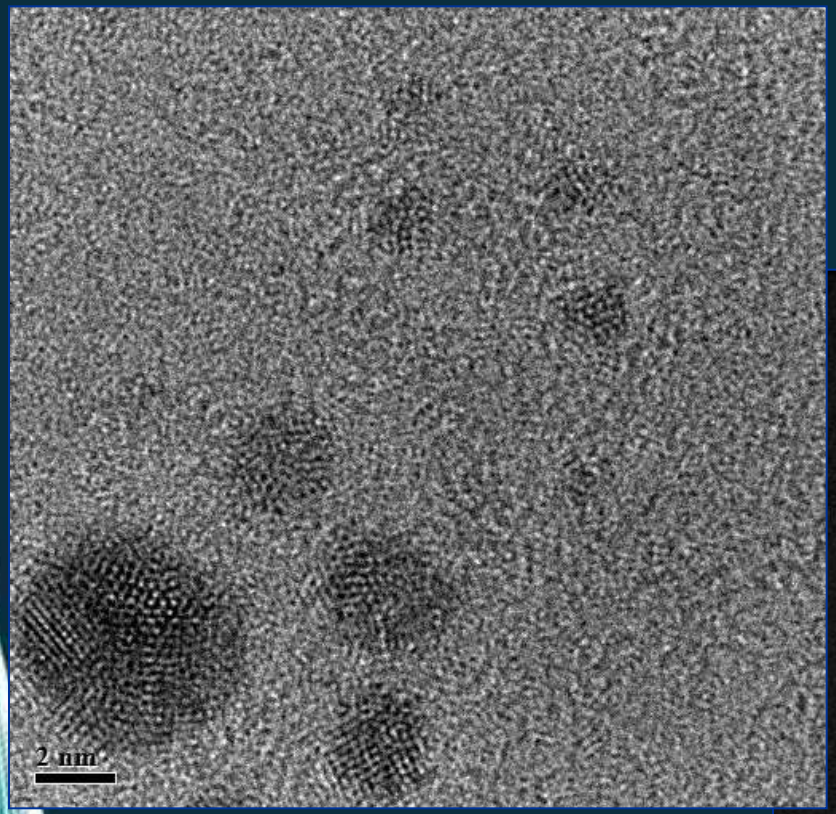


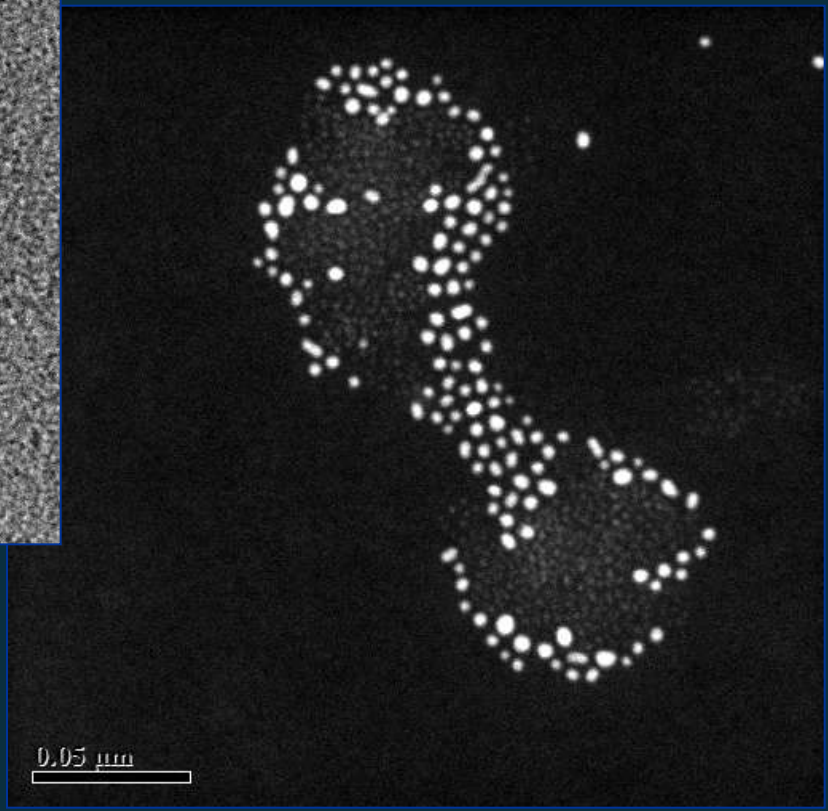

$Z_{Si} = 14$

**HAADF STEM Image**

$Z_{Sb} = 51$

# Bimetallic nanoparticles: alloys Vs. Core/shell




Cu/Au System

$Z_{Cu}$ = 29

$Z_{Au}$ = 79

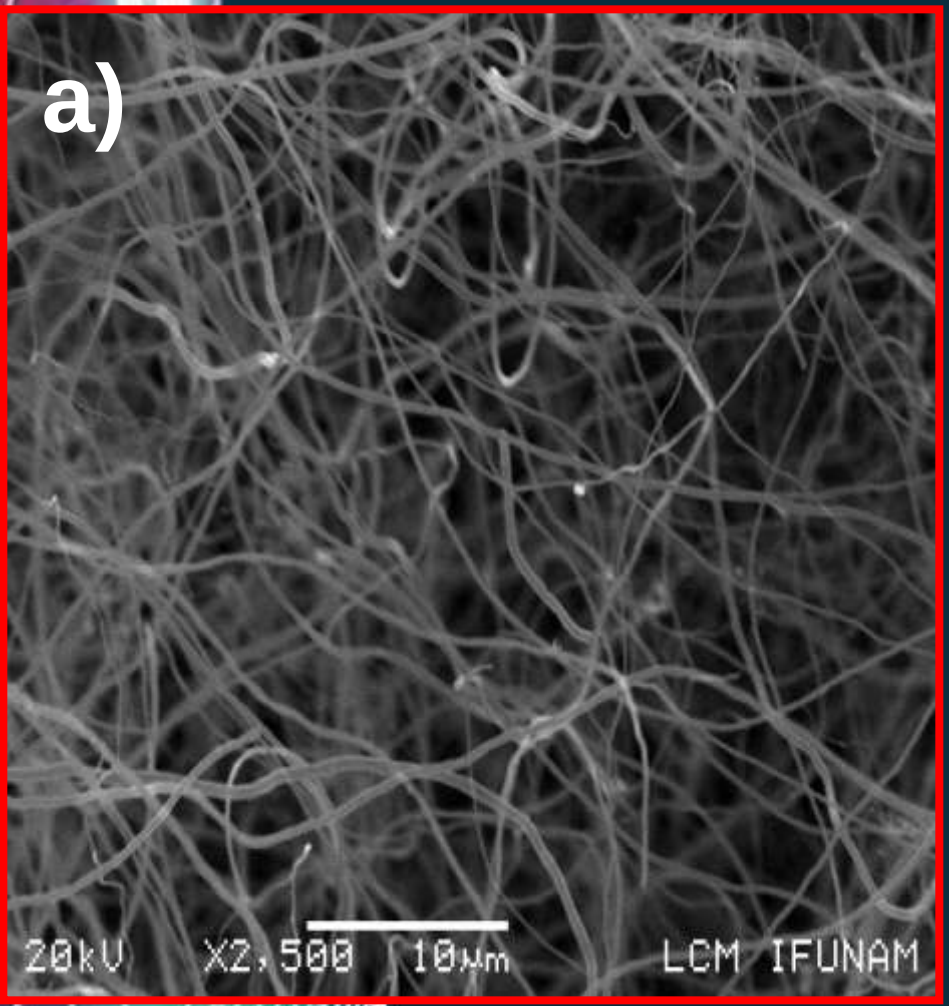
# Nanotubes doped with S

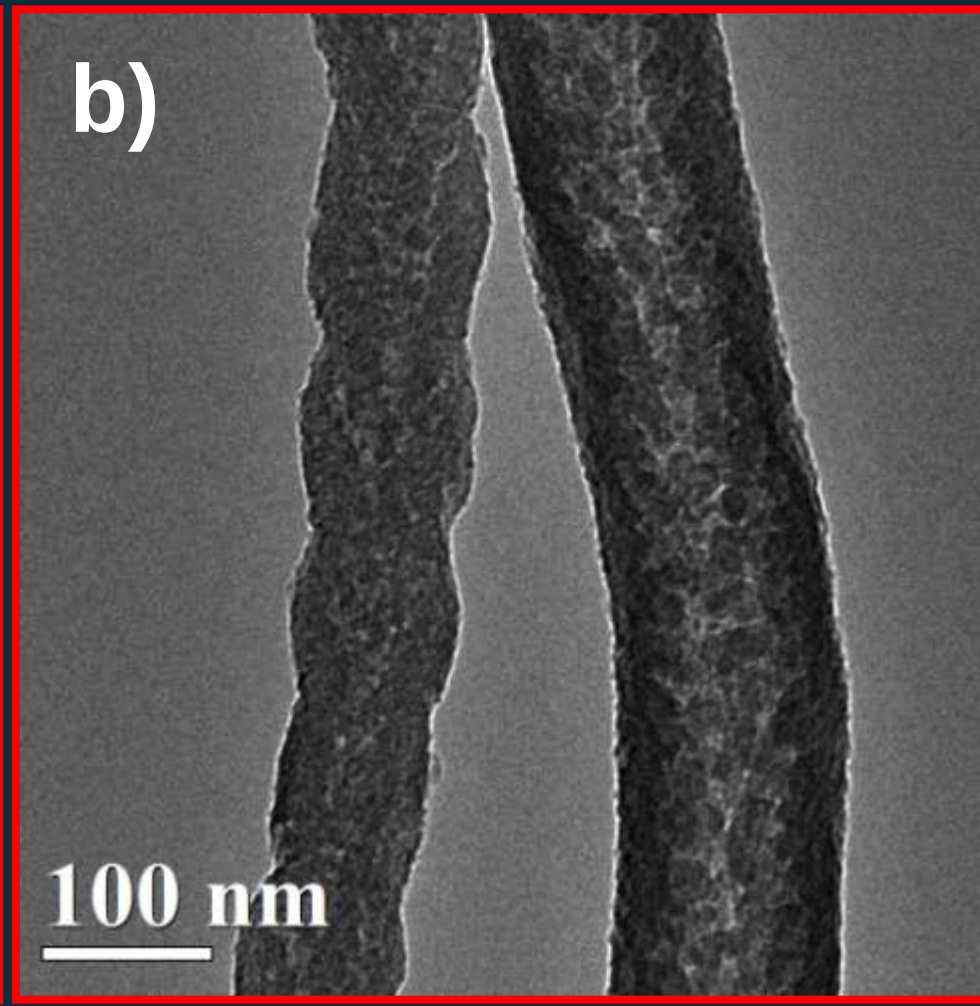
- Thermal Chemical Vapor Deposition (CVD)

**Thermal decomposition of organometalic precursors in controled atmosphere.**

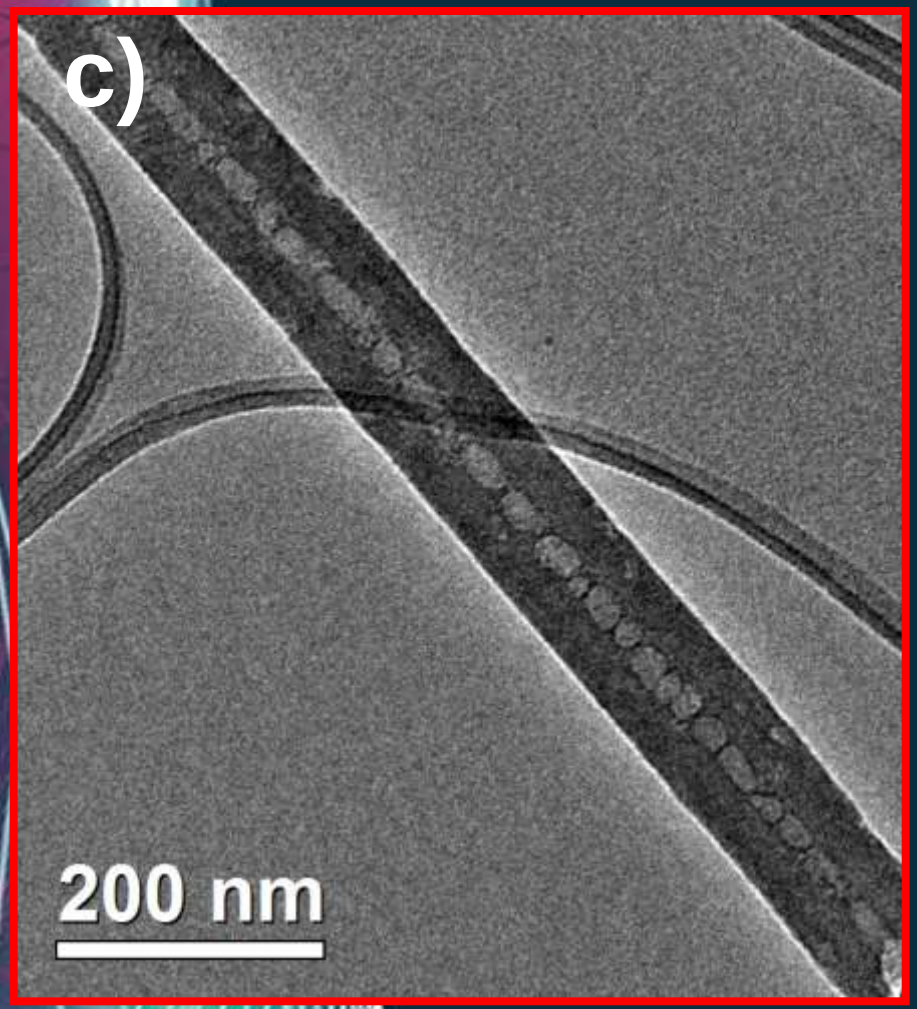
- Solution of Fe(NO3).9H2O in ethanol
- $CS_2$ source of S and C

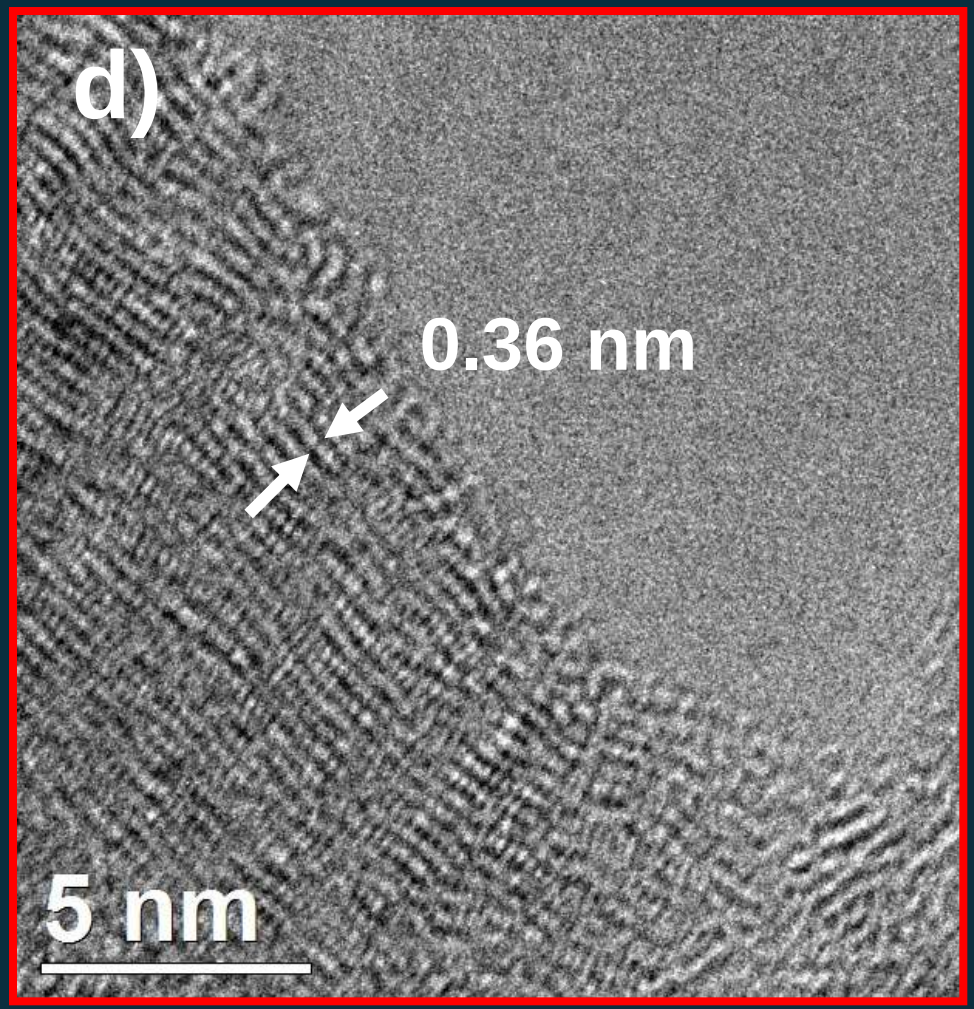
# Nanotubes doped with S



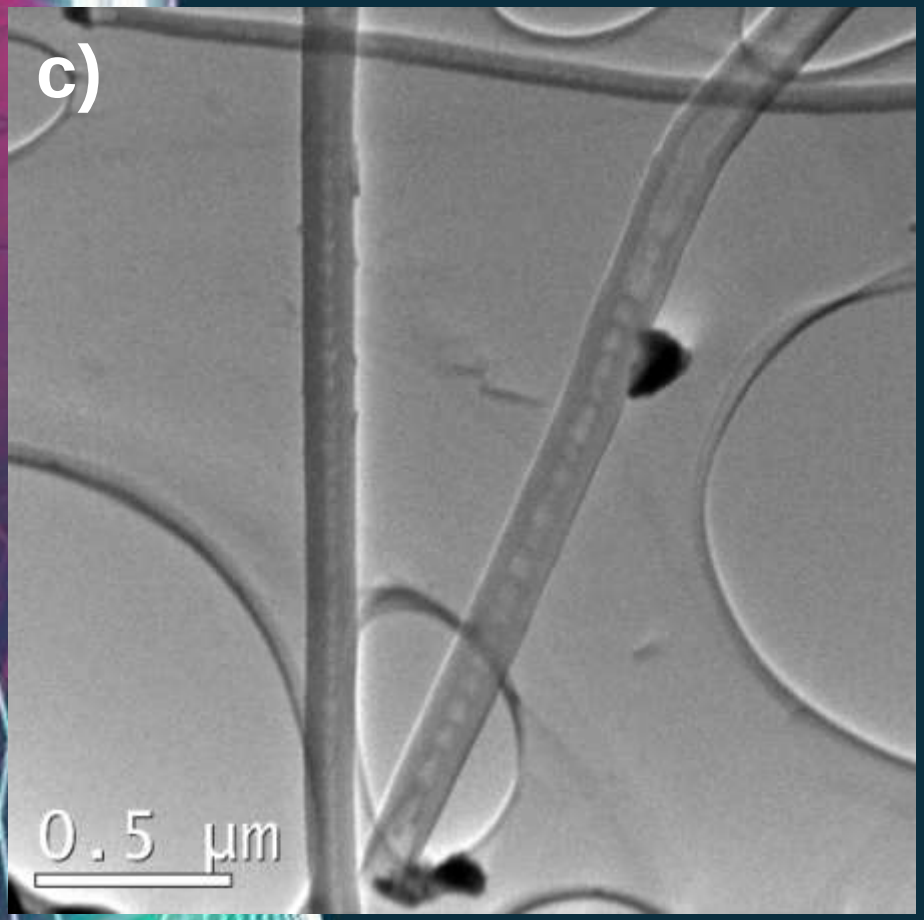



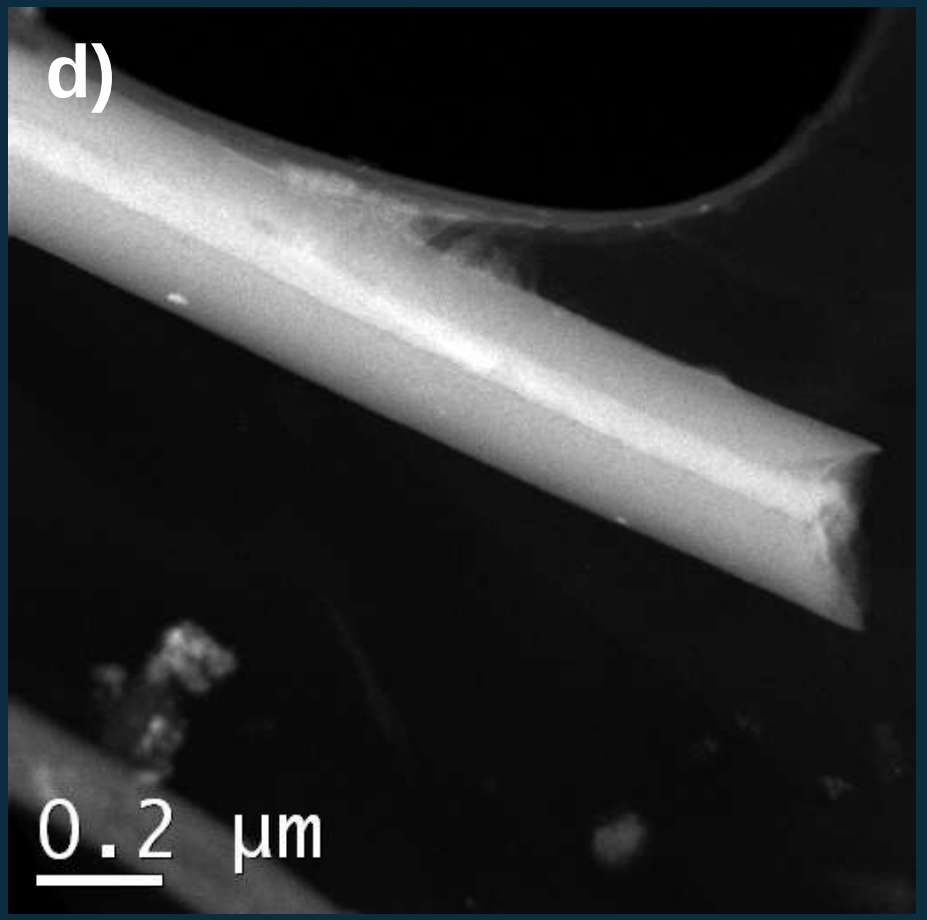
# Nanotubes doped with S



# Nanotubes doped with S



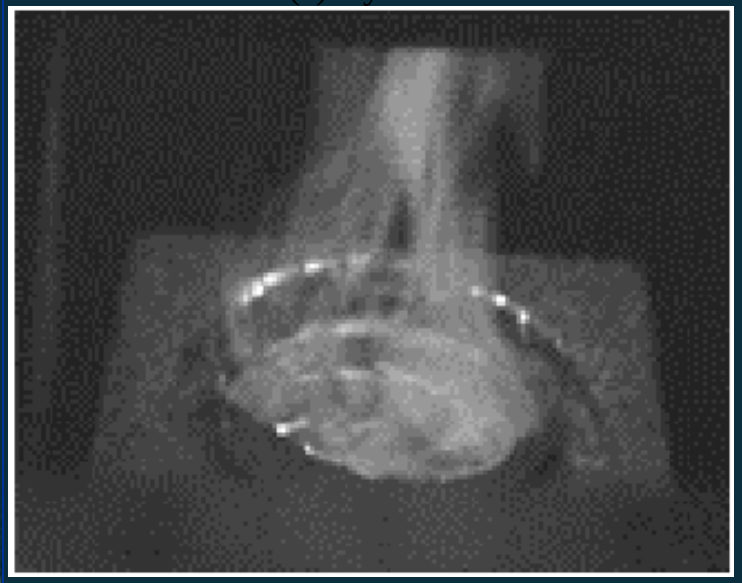

$Z_C = 6$
$Z_S = 16$

# Polymers and Soft Matter

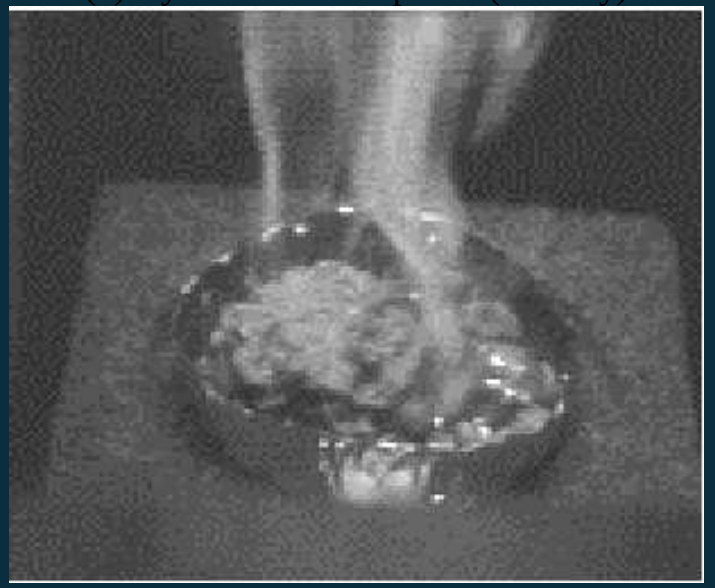
# Fire Retardation in Plastics

- Flammability and thermal stability studies of polymer layered silicate (clay) nanocomposites

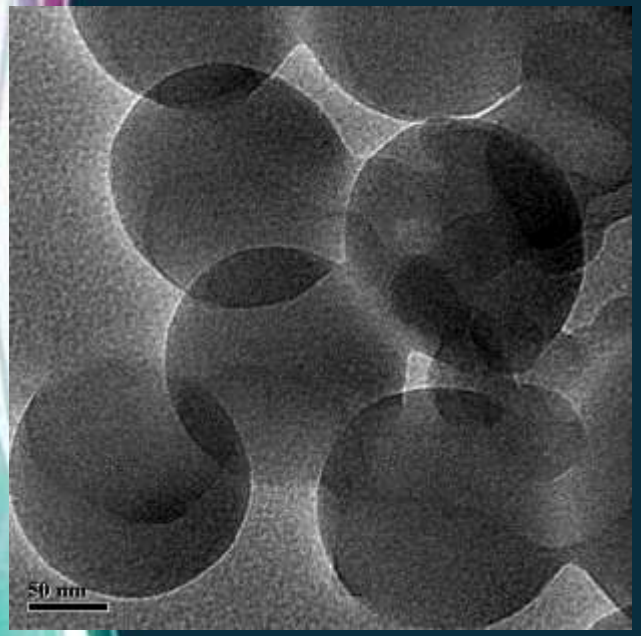
(a) Nylon 6

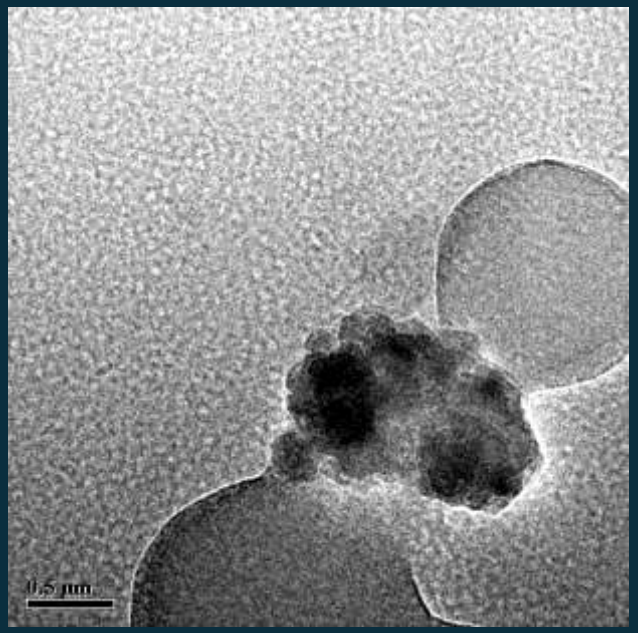


(b) Nylon 6 nanocomposite (5% clay)

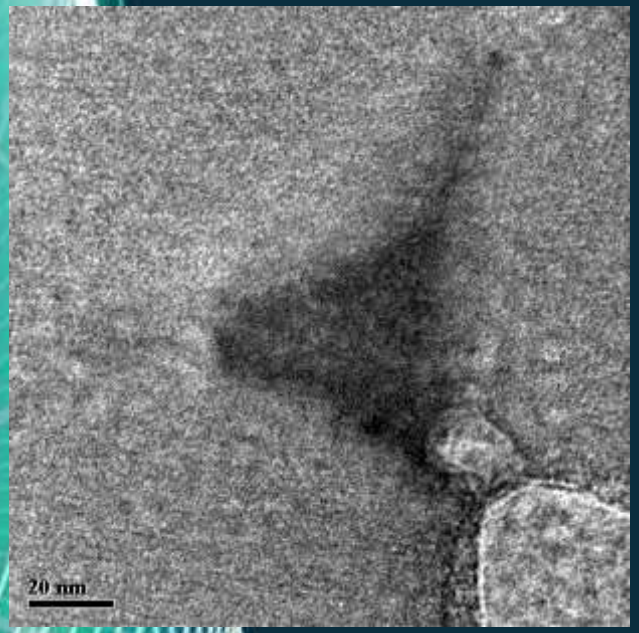


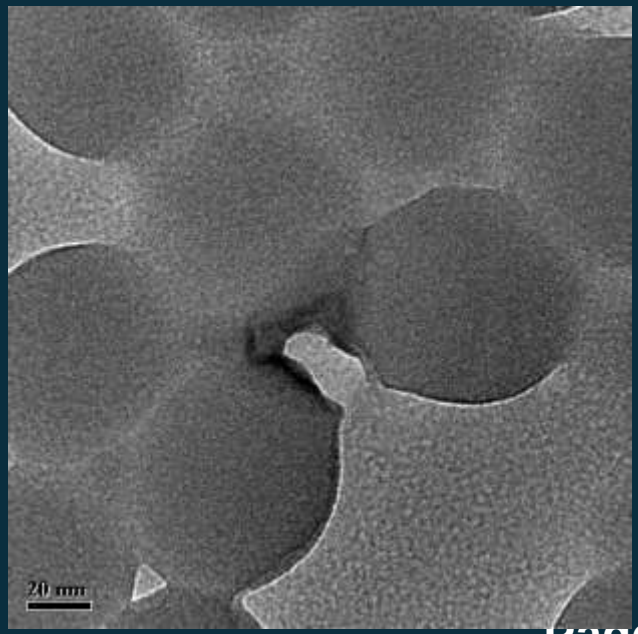
Source: IWGN (1999/09), Gilman 1999

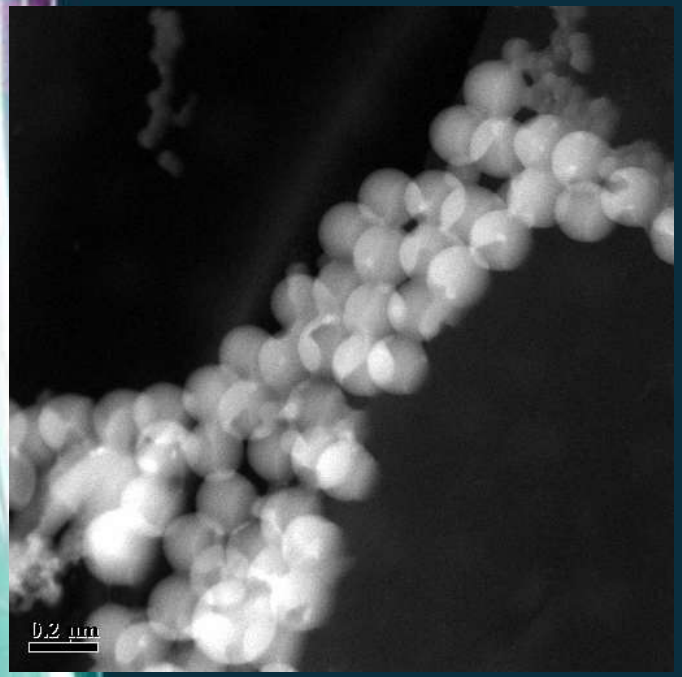


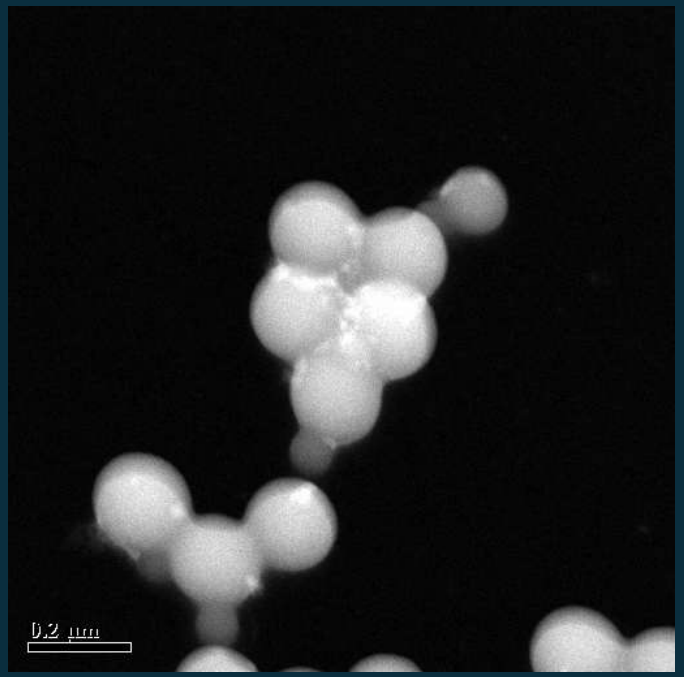




DADMAC

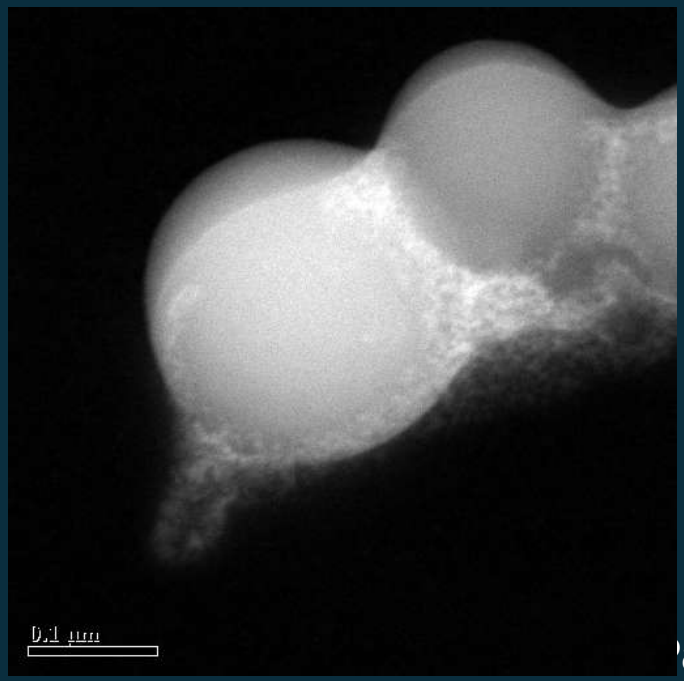


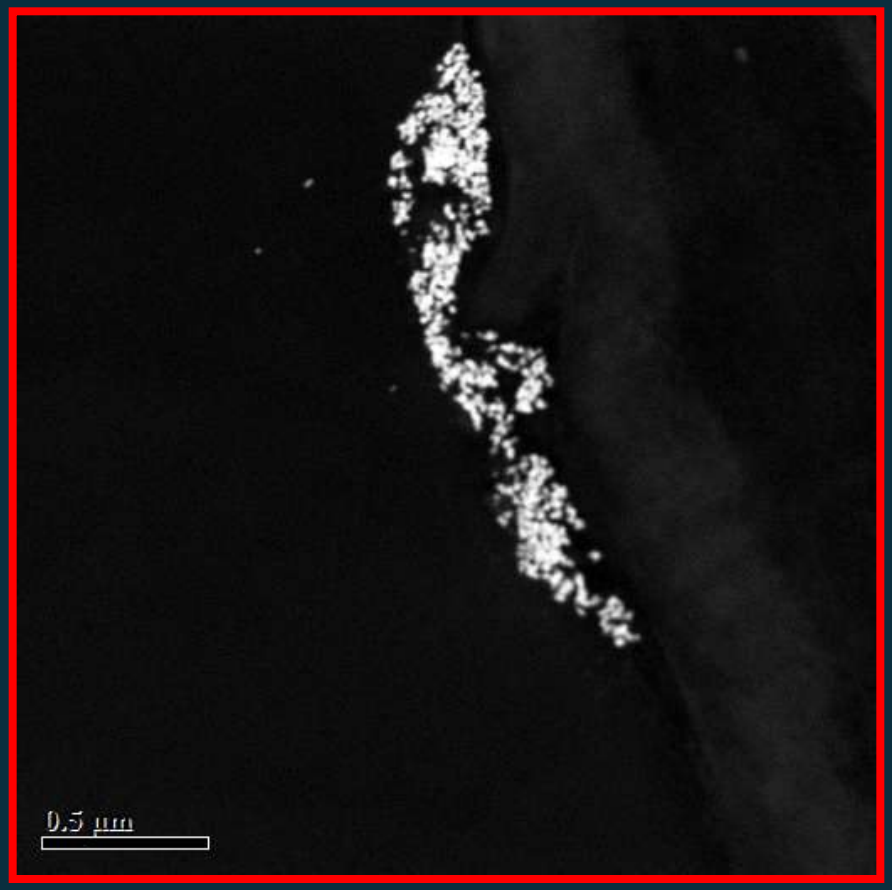

0.2 µm

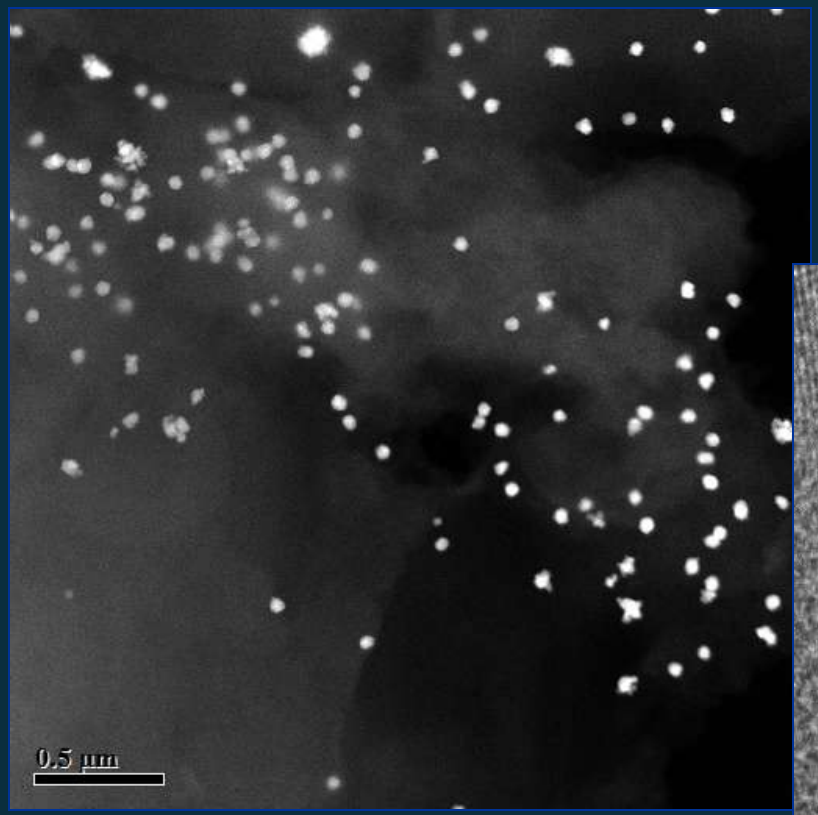

0.2 µm

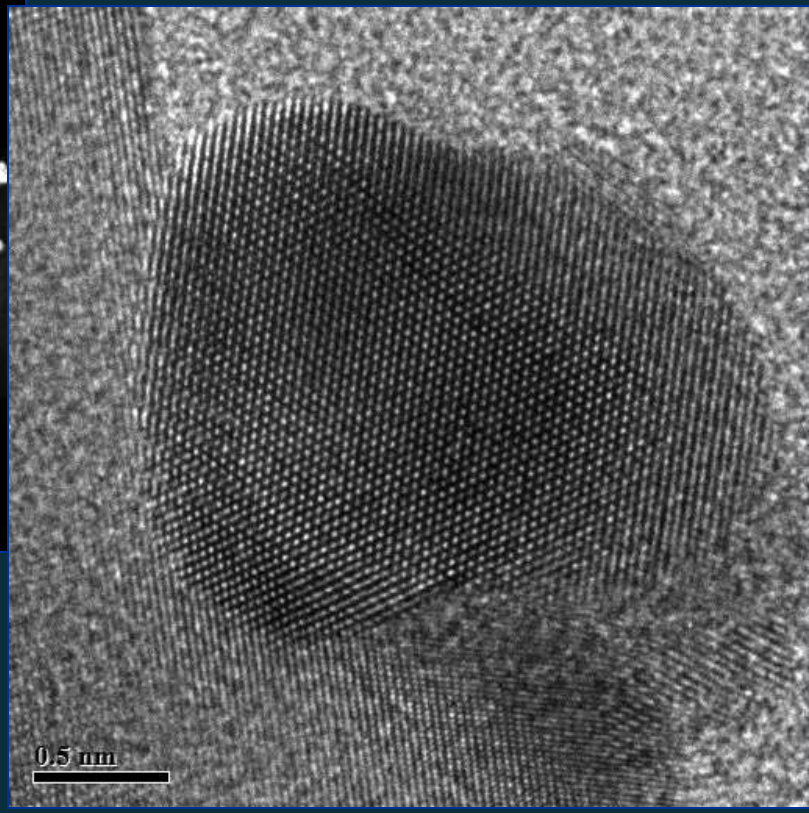

0.2 µm


0.1 µm

# Au nanoparticles Bio-reduction by an alive alfalfa plant

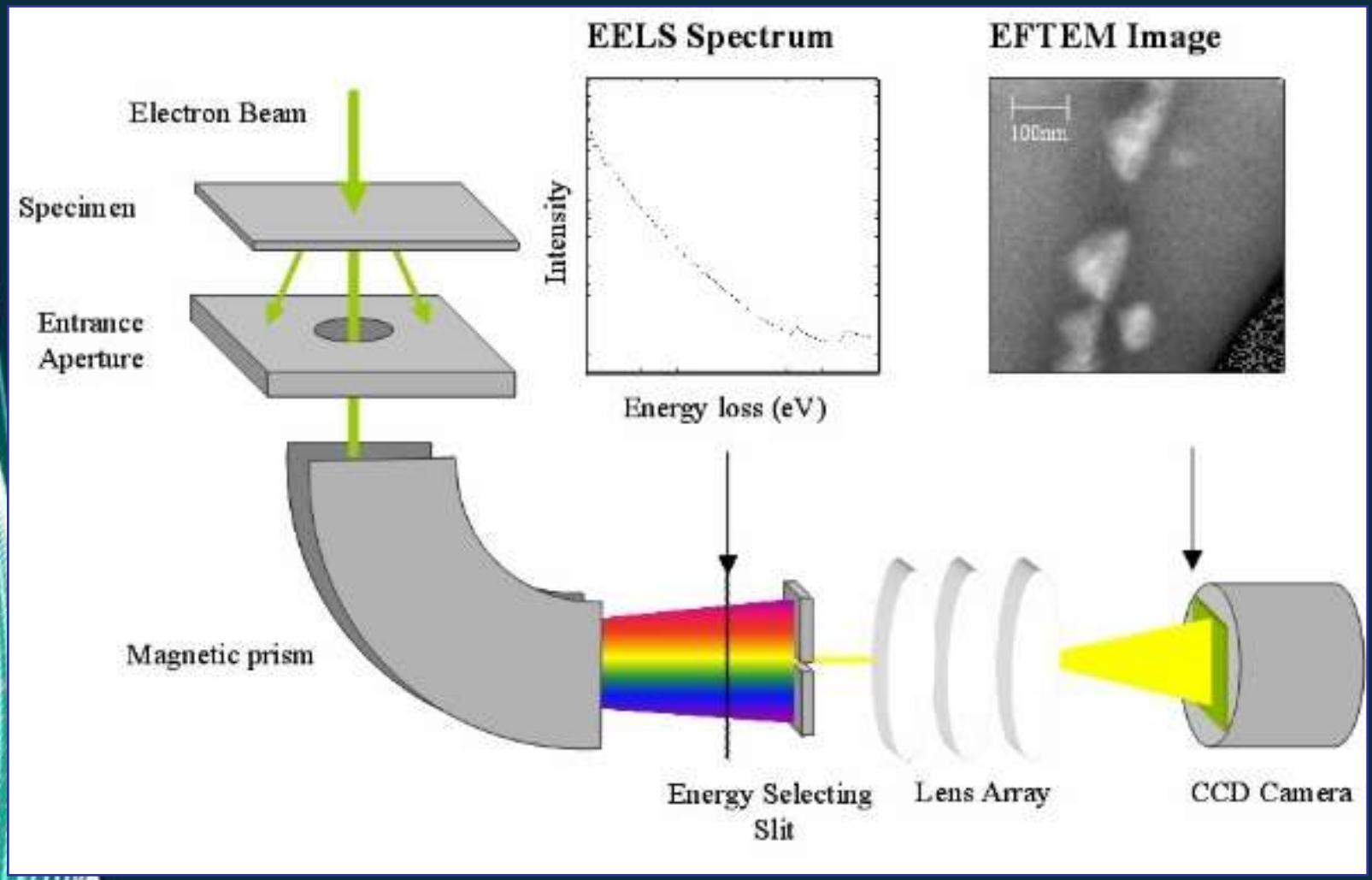




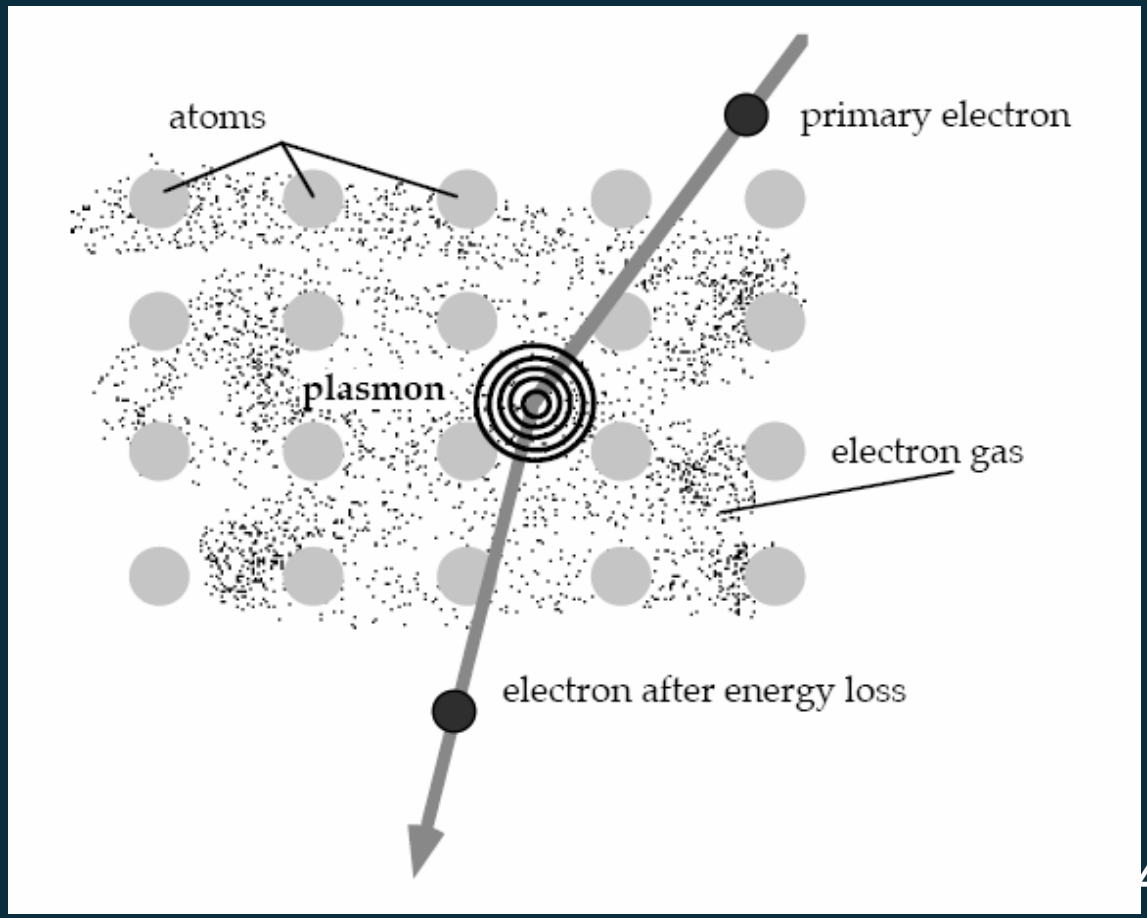



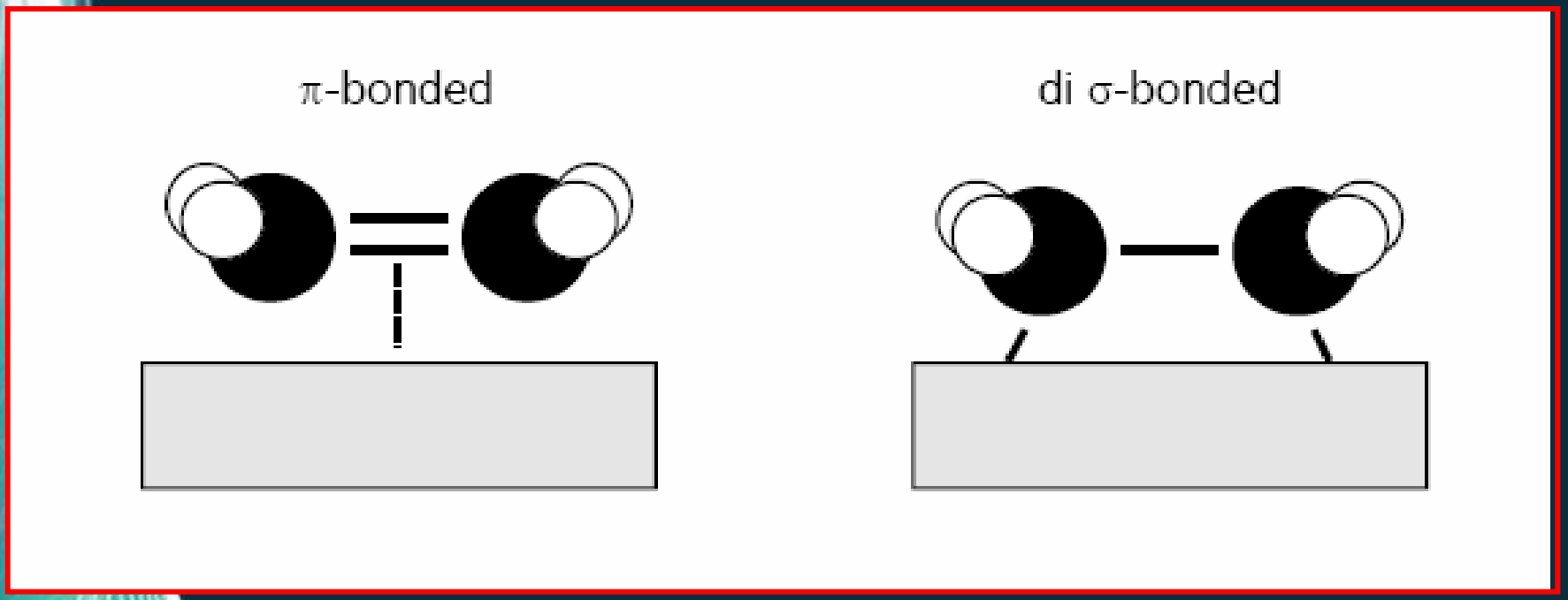

Au nanoparticles bio-reduction by avena biomass.
Journal of Nanoparticle Research, 6, 4, 377-382. 2004

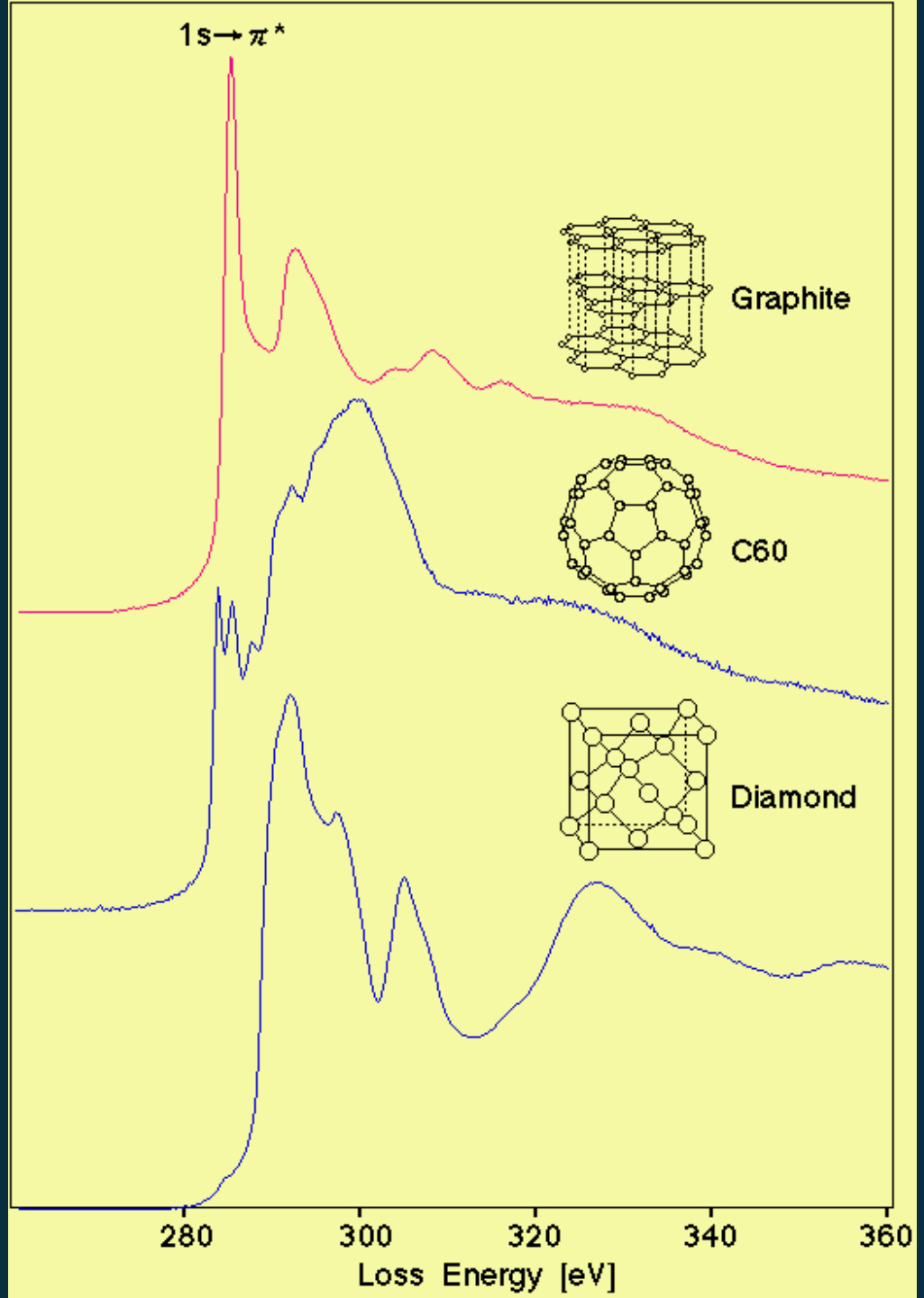
# Gatan Image Filter EELS



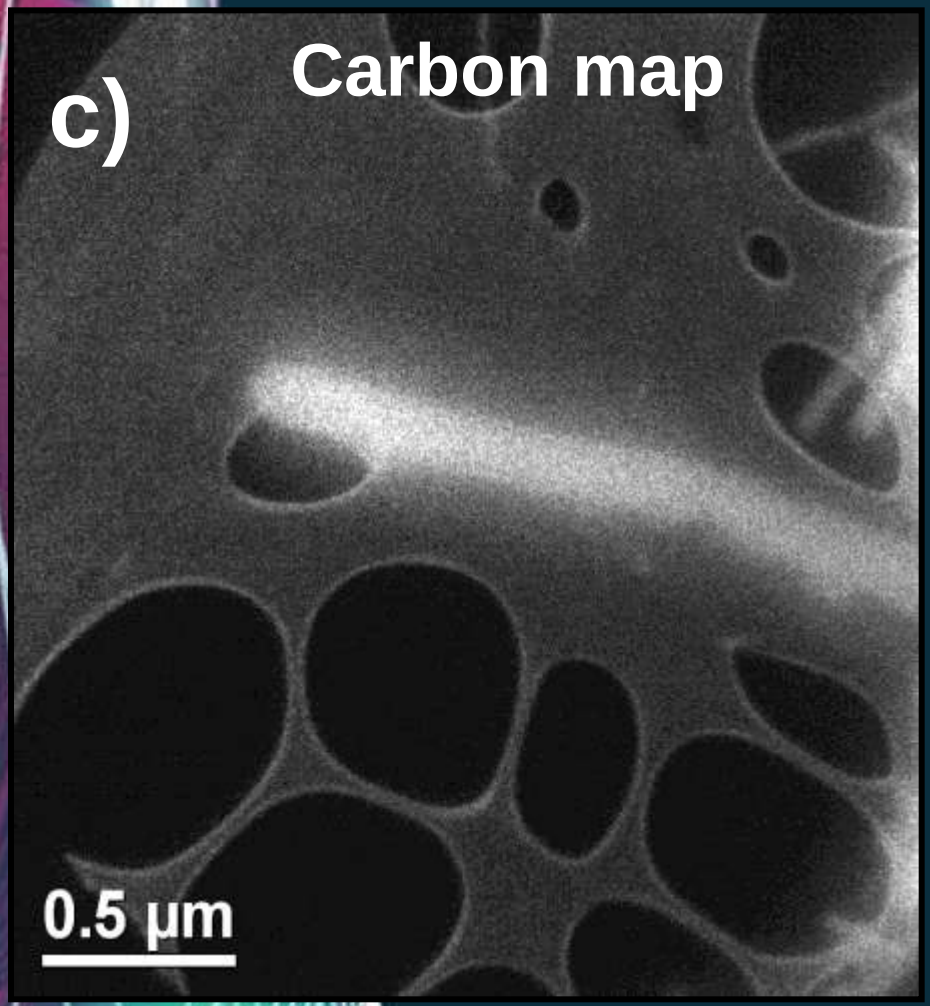
# 1. Plasmons
– vibration of an electron gas
– corresponding quasi particles: plasmons

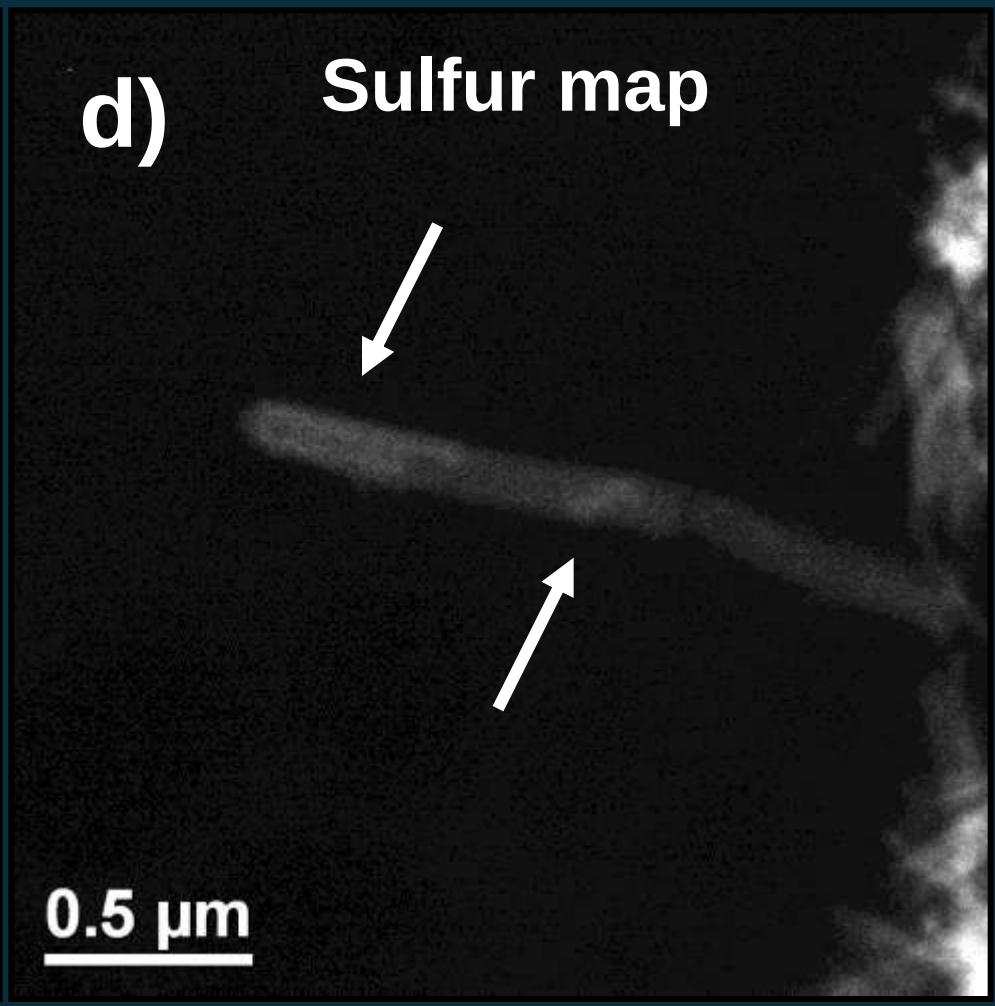



π-bonded
di σ-bonded


1s→π*
Graphite
C60
Diamond
280
300
320
340
360
Loss Energy [eV]

# Nanotubes doped with S



# Colaboradores:

Dr. Thomas Buhse
Dr. Germinal Cocho
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