



# Advanced Microscopy

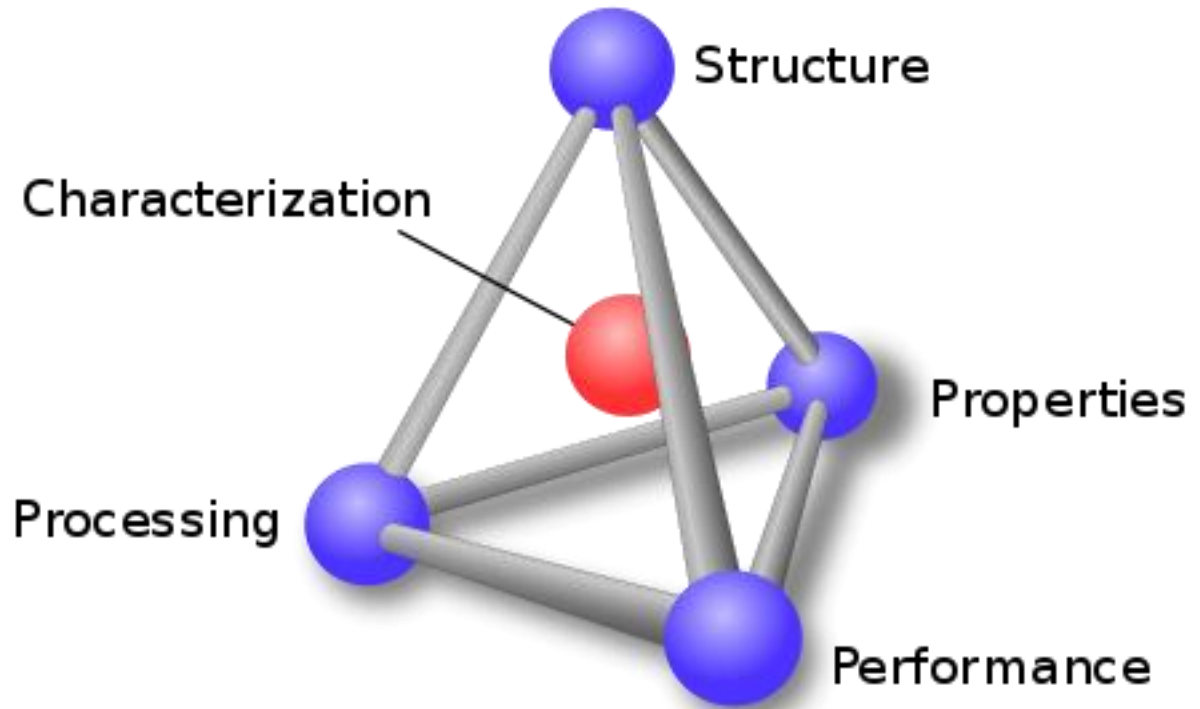
Dr. Chanchana Thanachayanont



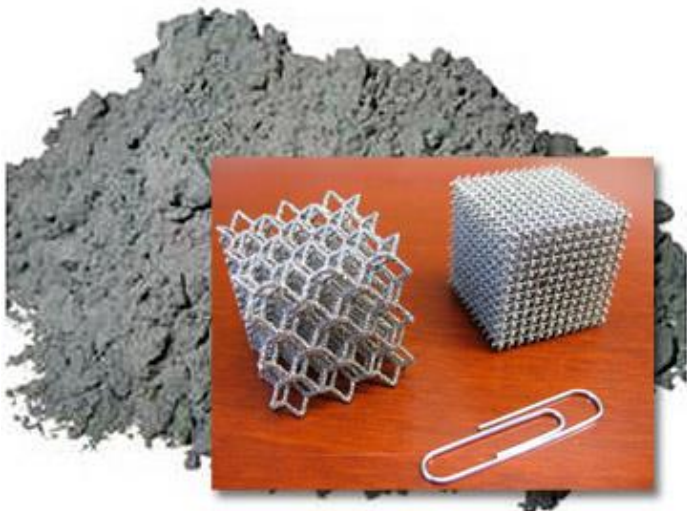


# Outline

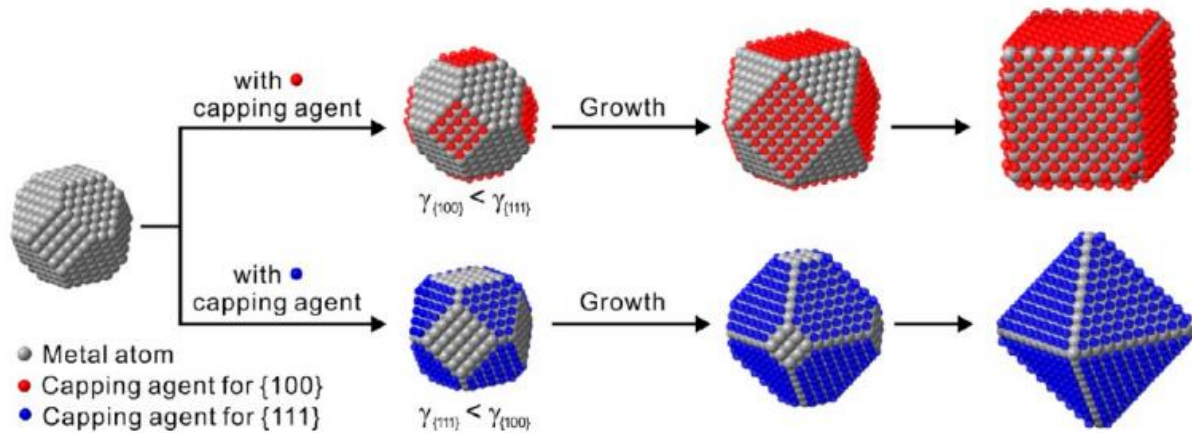
- Overview
  - Impression
  - Related characterization techniques
  - Point of view
- Fundamentals
- Research examples
- Conclusion



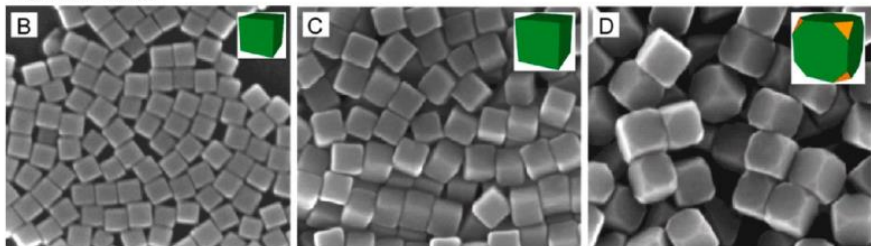
[https://en.wikipedia.org/wiki/Materials\\_science](https://en.wikipedia.org/wiki/Materials_science)



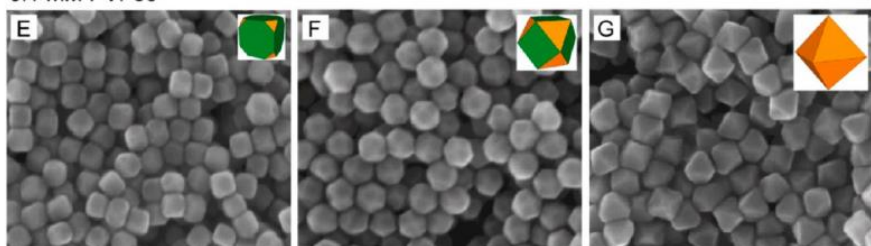
# Examples



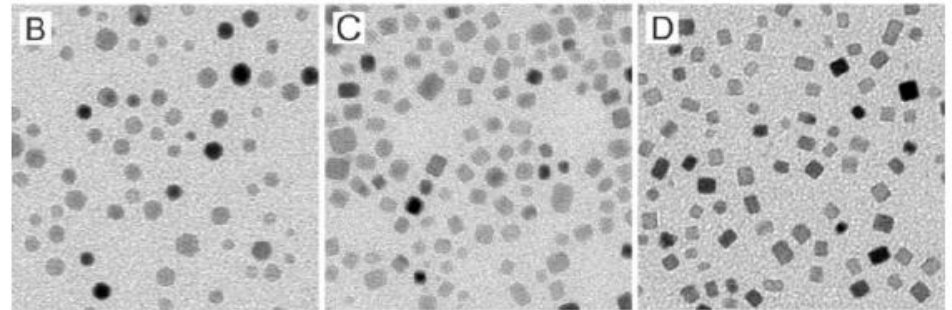
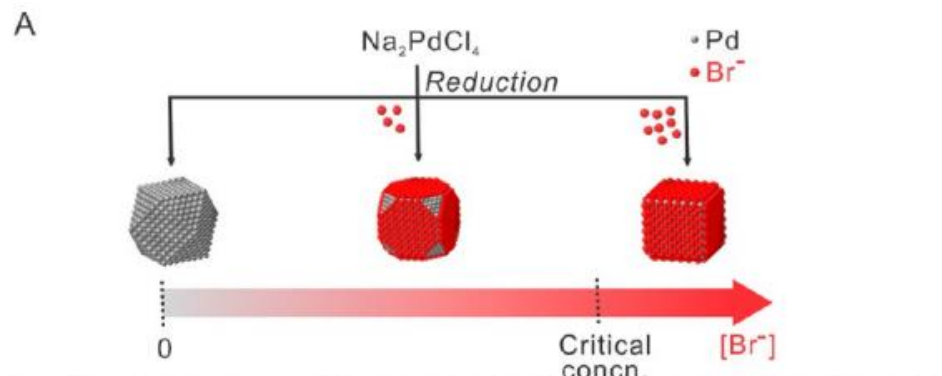
1.0 mM PVP55



0.1 mM PVP55





— 100 nm



— 20 nm

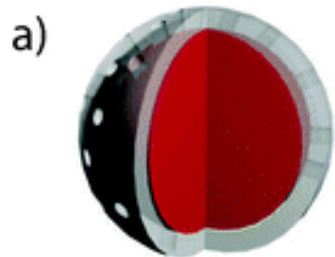
# Heterogeneous Nanostructured Materials with Different Morphologies

0-D 

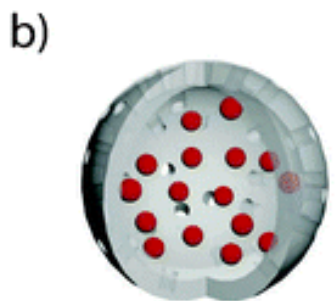
1-D 

2-D 

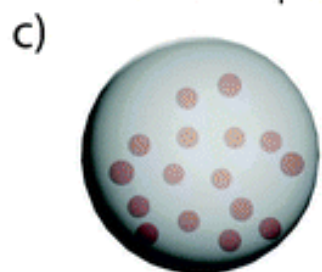
3-D 



Core-Shell Nanoparticle



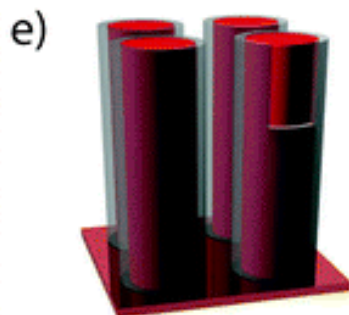
Nanoparticles Encapsulated in Hollow Nanosphere



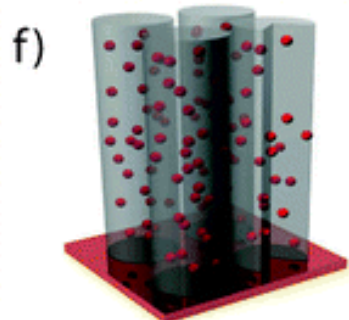
Composite Nanoparticle



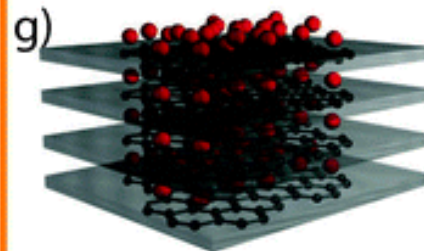
Carbon Nanotube Based Composite Electrode



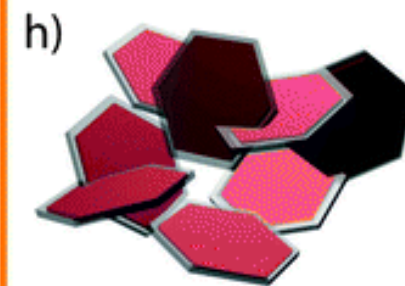
Coaxial Nanowire Array



Composite Nanowire Array



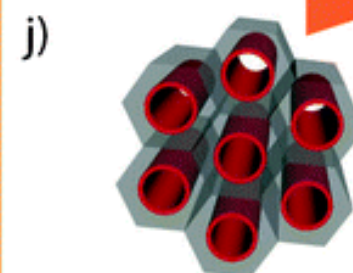
Graphene Based Composite



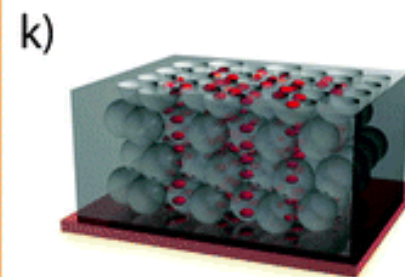
Carbon Coated Nanoplates



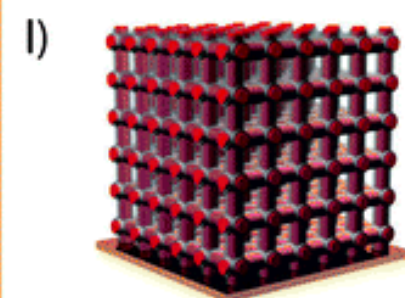
Carbon Coated Nanobelts



Mesoporous Composite Electrode



Microporous Composite Electrode



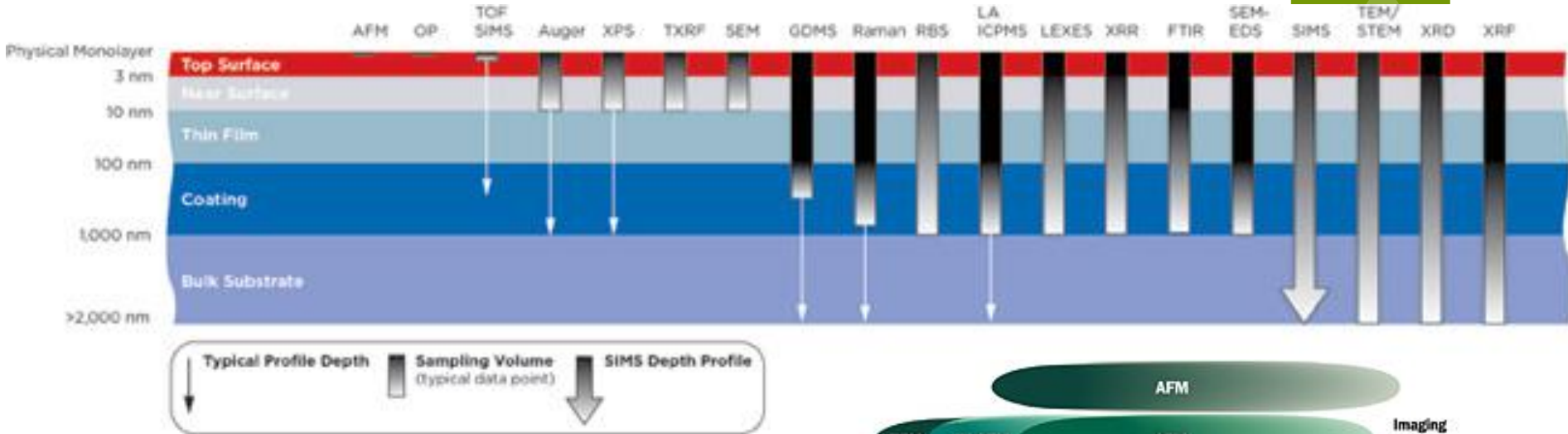
Future 3-D Electrode

Liu et al.

*Chem. Commun.*, 2011,47, 1384-1404



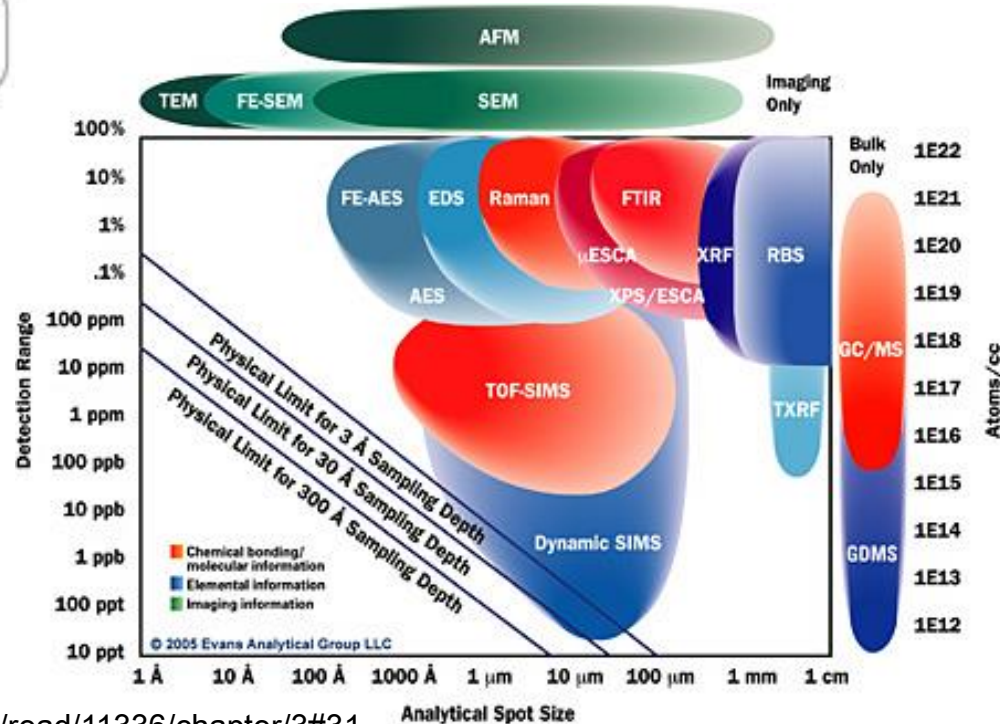
# Advanced Materials Characterization



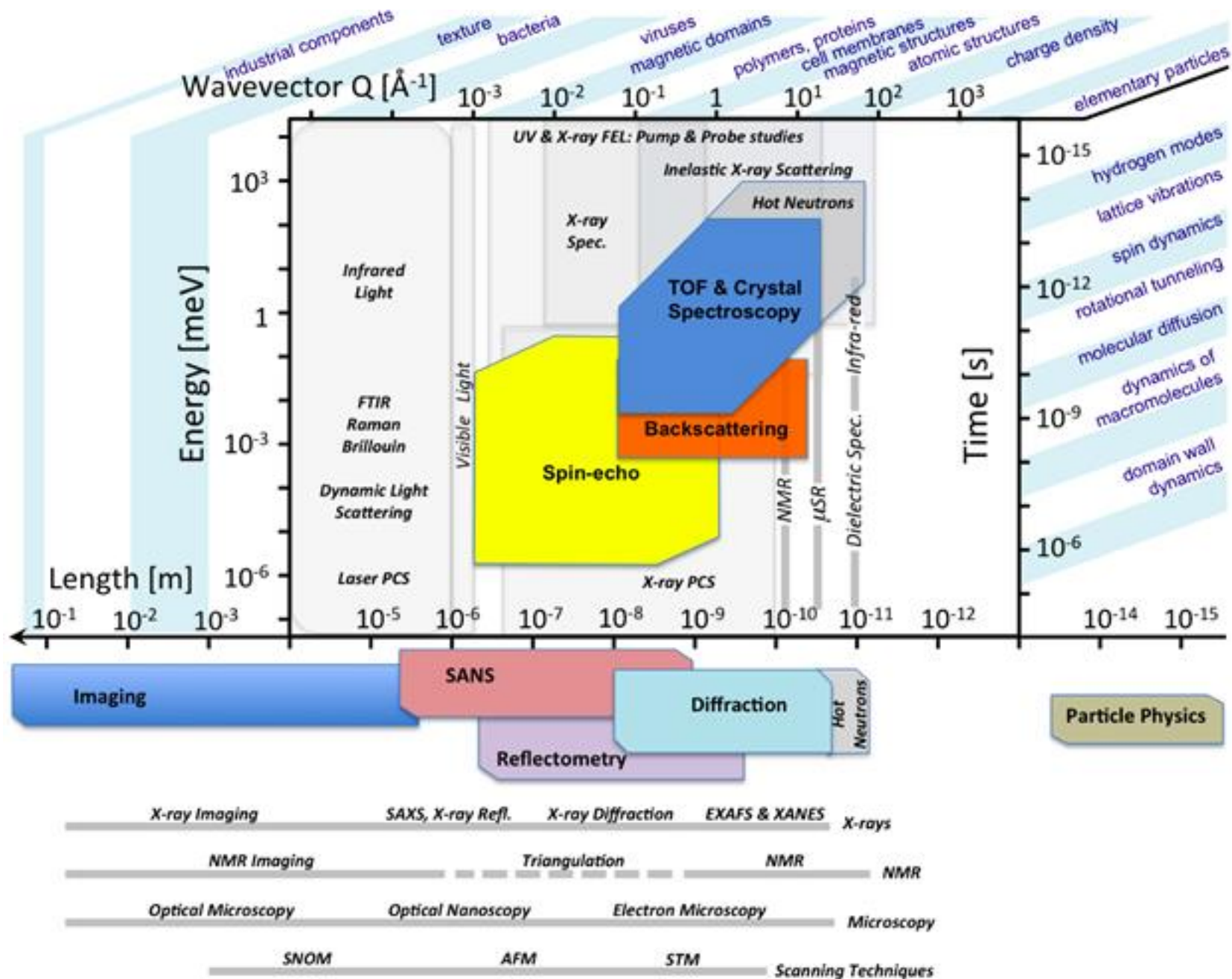
<http://www.eag.com/mc/thin-film-analysis.html>

Surface	Up to 1 nm	(1-3 atomic layers)
Ultra-thin film	1 to 10 nm	(3-30 atomic layers)
Thin film	10 nm to 2 $\mu\text{m}$	(30-600 atomic layers)
Bulk	>2 $\mu\text{m}$	(>600 atomic layers)

<https://www.mccrone.com/mm/surface-analysis/>



<http://www.nap.edu/read/11336/chapter/3#31>



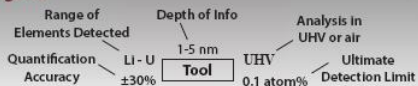


# Feature-Problem-Analysis-Tools

## Visual Guide to Selecting Tools for Chemical Analysis\*

**Legend for Tool**  
Major Applications  
Type of Chemistry Info  
XY Map, Profile or Angles  
Other Applications  
Not good for...  
Chemical State (Yes/No)  
Measures thickness

**Legend**



### Bulk Info

**Molecular Bonding**  
0.5-2.0 μm in air  
±10%  
**FT-IR**  
0.1 wgt%  
Contamination, QC Organics, Silicon  
Fingerprint Identification  
Film Thicknesses  
AT-FT-IR for Surface Films  
Not for metals or alloys

**Al - U**  
0.1-0.5 μm in air  
±10%  
**XRF**  
PPM  
Bulk Analysis, Alloy ID  
Film Thicknesses (1-5 μm)  
No Chemical States

**Li - U**  
~1 μm UHV  
±50%  
**LA-ICP-MS**  
PPB  
Contamination, Unknowns, FA  
Conductors, Semicon, Insulators  
Measured Elemental Ions  
~1 micron per laser pulse  
No Chemical States

### Depth Profiling Info

**Li - U**  
5-20 Å UHV  
±50%  
**D-SIMS**  
PPM  
Isotope analysis, Dopant Profiles  
Semiconductor Films  
Element versus Depth info  
Profile Speed: <0.01 micron/min  
Usually 5-20 elements per profile  
Etch Depth Resolution 5-10 Å  
Molecular fragments

**H - U**  
2-10 Å 1 torr  
±10%  
**GD-OES**  
PPM  
Multi-Layer Films, Silicon Re-cycle  
Bulk, PV, Trace element, Unknowns  
Profile Speed: up to 10 micron/min  
50 elements per profil  
Element versus Depth info  
Monolayer resolution  
Excellent Quantitative Results  
Etch Depth Resolution 2-10 Å  
Final etch depth ~200 μm  
No molecular fragments

### Surface Info

**Li - U**  
1-5 nm UHV  
±30%  
**FE-Auger**  
0.1 atom%  
Particles, Defects, FA  
Contamination, Unknowns  
Conductors, Semicon (Insulator)  
Chemical States (Si vs SiO2)  
XY Map, Depth/Line Profiling  
Angle Resolve AES: 1-5 nm  
Ar+ Ion Cleaning inside  
Final etch depth ~1 μm  
Insulators need charge neutralizer  
and high tilt angle

**Li - U**  
1-12 nm UHV  
±5%  
**XPS**  
0.1 atom%  
Surface Contamination, Thin Films  
Powders, Greases, Glove Contam.  
QC, QA, FA, Unknowns  
Conductors, Semi, Insulators  
Chemical States (Si vs SiO2)  
XY Map, Depth/Line Profiling  
Angle Resolve XPS: 1-10 nm  
Ar+ Ion Cleaning inside  
Final etch depth ~1 μm  
Insulators need charge neutralizer

**H - U**  
2-6 Å UHV  
±50%  
**ToF-SIMS**  
PPB  
Monolayer Contamination  
Conductors, Semi, Insulators  
Molecular Fragments  
XY Map, full spectrum each pixel  
Ga+ Ion Cleaning inside  
Final etch depth ~100 nm  
Insulators need charge neutralizer

### Sub-Surface Info

**Molecular Bonding**  
0.2-2.0 μm in air  
±10%  
**μ FT-IR**  
0.5 wgt%  
Contamination (>0.2 μm)  
Organics, Silicon  
No Metals or Inorganics  
Molecular Bonding  
Fingerprint Identification  
XY Map, Confocal Profiling  
Not for metals or alloys

**Be - U**  
0.3-3.0 μm UHV  
10%  
**EDX - SEM**  
1 atom%  
Sub-Surface Elements, Particles  
>300 nm Thick Contamination  
Unknowns  
No Chemical States  
XY Sub-Surface Map  
UHR-SEM Imaging  
Insulators need Au coating

**Molecular Bonding**  
0.5 - 5.0 μm in air  
±10%  
**Raman**  
0.1 wgt%  
Particles, Contamination, Films  
Organics, Inorganic  
Molecular Bonding  
Carbon Phases (diamond)  
Stress, Orientation  
Film Thicknesses  
Confocal Profiling  
Not for metals or alloys

### Ion Milling Info

Etch Depth: 0.1-100 μm UHV  
**FIB/Dual-Beam**  
Used to mill a trench by using Ga+ ions to expose multiple layers or to cut a defect in half exposing the inside for EDS, TEM or Auger analysis.

### Buried Layer Info

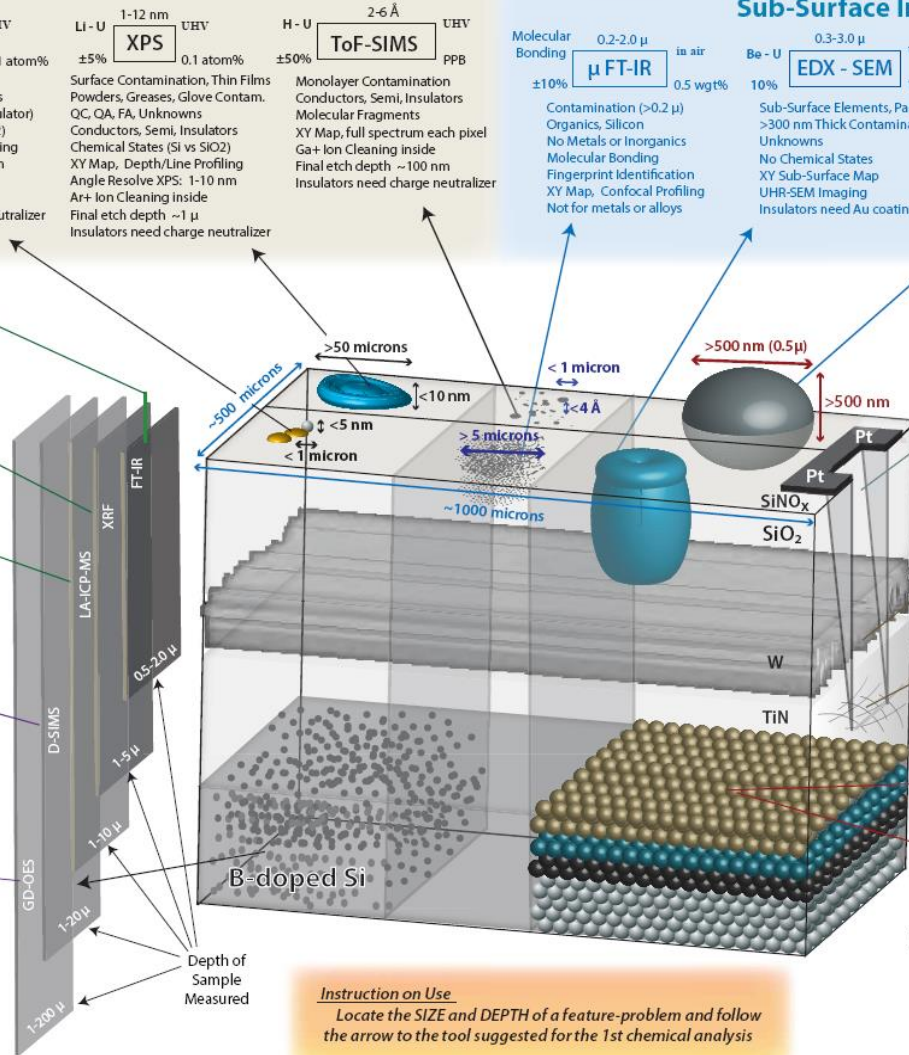
**3-10 nm in air**  
~1% of thickness  
**XRR**  
Crystalline Materials, Semicon  
Film Thicknesses  
Thickness of layers must be >3 nm  
Density of buried layers  
Roughness of interfaces  
Need 10-20 mm length (1 mm width)

**10 nm-1 μm in air**  
~5%  
**XRD**  
Crystalline Materials, Semicon  
Stress, Identify Phase  
Texture orientation  
Degree of crystallinity  
Size of crystallites  
% of amorphous nature  
Solid materials only

### Atomic Scale Info

**Al - U**  
2-100 nm UHV  
±20%  
**TEM-EDX**  
0.5 atom%  
Defects, Atomic layers (>2nm)  
Particles, Unknowns  
Element Maps, Line Profiles  
TEM Imaging  
No Chemical States

**Li - Mg**  
0.8-100 nm UHV  
±20%  
**STEM/TEM-EELS**  
0.5 atom%  
Defects, Atomic layers (>0.8 nm)  
Particles, Unknowns  
Element Maps, Line Profiles  
STEM/TEM Imaging  
No Chemical States



**Instruction on Use**  
Locate the **SIZE** and **DEPTH** of a feature-problem and follow the arrow to the tool suggested for the 1st chemical analysis

**Analysis Modes that Measure In X-Y and Z**  
Point Mode Spectra  
Angle Resolve Profile  
Line Profile  
Depth Profiles  
XY Mapping

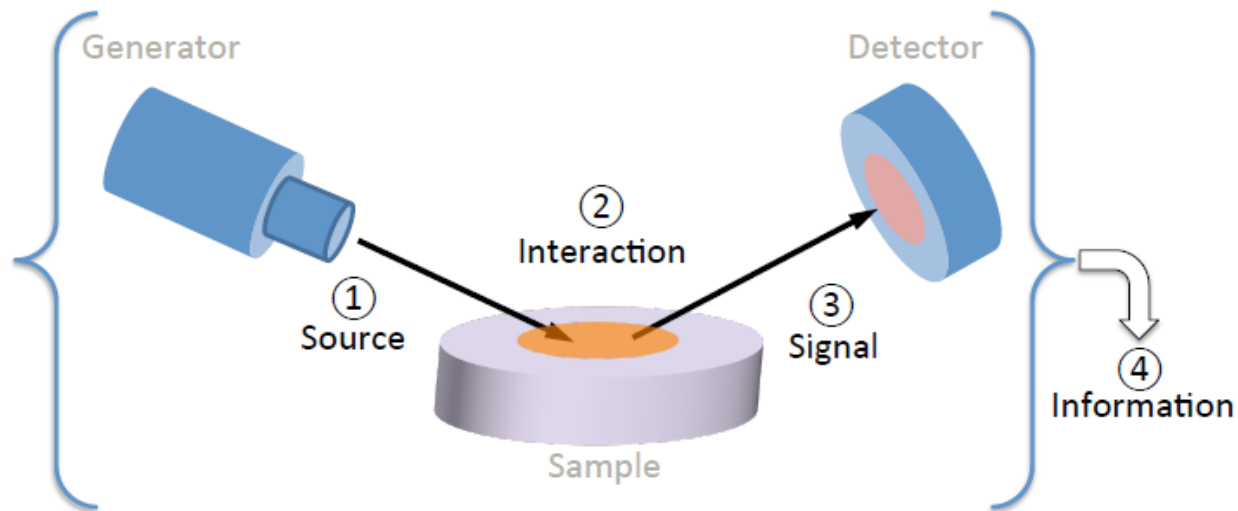
\* This guide helps the user to select the first chemical analysis tool to analyze or measure the feature-problem. Additional analysis tools are often used to confirm or further understand the feature-problem.



# Materials Characterization



## Basic Principle



- ① A source radiation is aimed at the sample
- ② It interacts with the sample in some way
- ③ As a result of the interaction, a signal is produced
- ④ Analysis of the signal reveals information about the sample

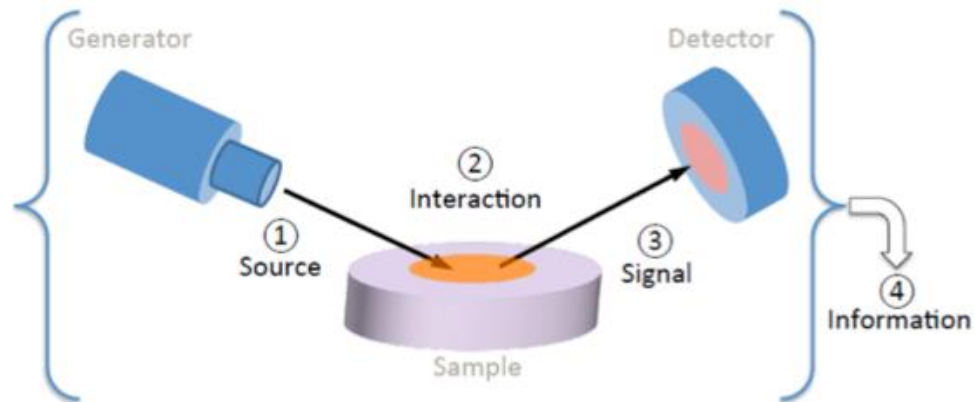


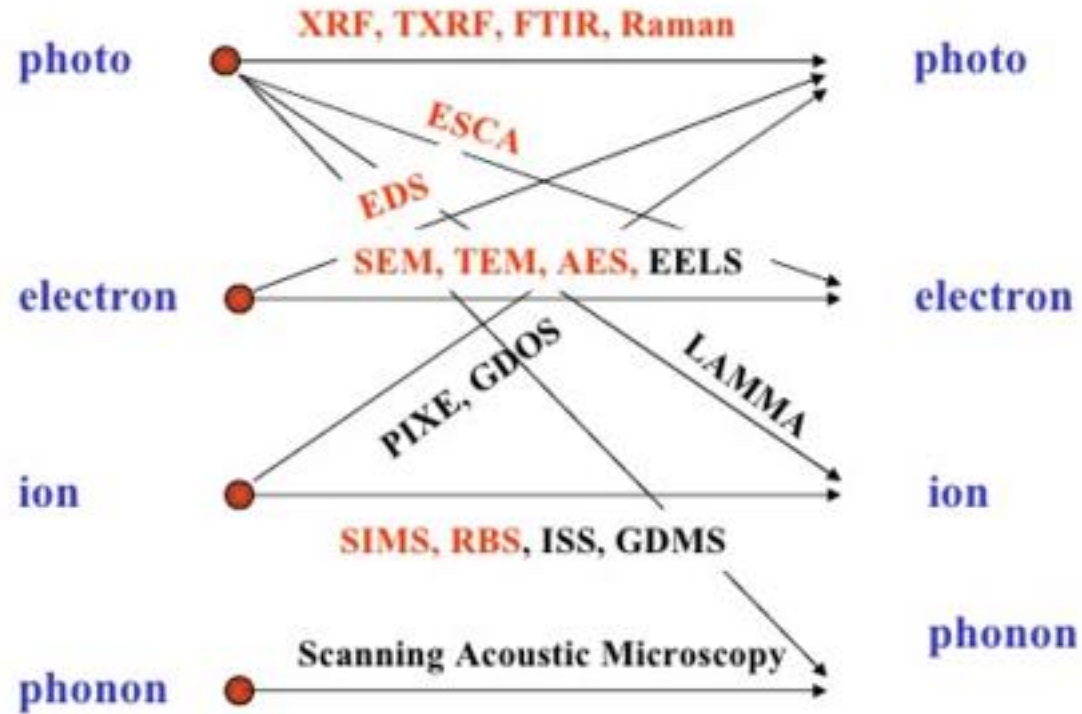
## Source

- Photon
- Electron
- Ion
- phonon

## Signal

- Photon
- Electron
- Ion
- phonon







# Advanced Microscopy



## Super-Resolution Microscopy Tutorial

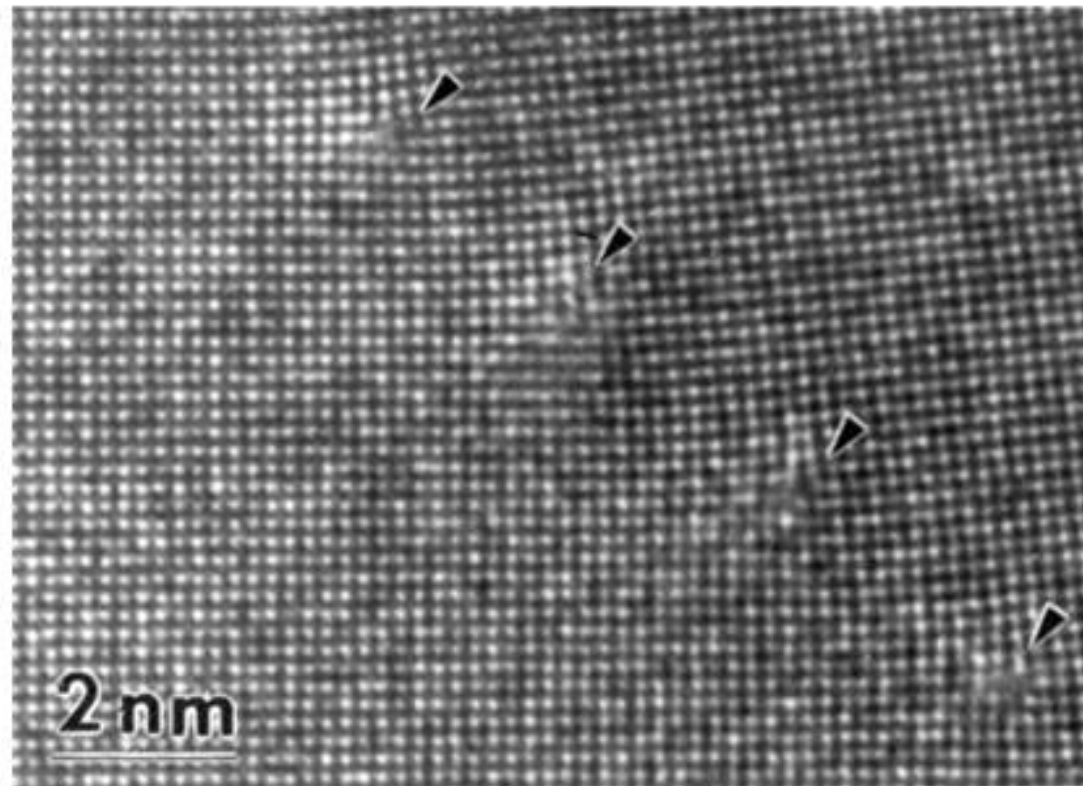
### Overview

Super-resolution microscopy is a collective name for a number of techniques that achieve resolution below the conventional resolution limit, defined as the minimum distance that two point-source objects have to be in order to distinguish the two sources from each other. There are two closely related values for the diffraction limit, the Abbe and Rayleigh criteria. The difference between the two is based on the definition that both Abbe and Rayleigh used in their derivation for what is meant by two objects being resolvable from each other. In practical applications, this difference is small. The Abbe criterion is defined as:

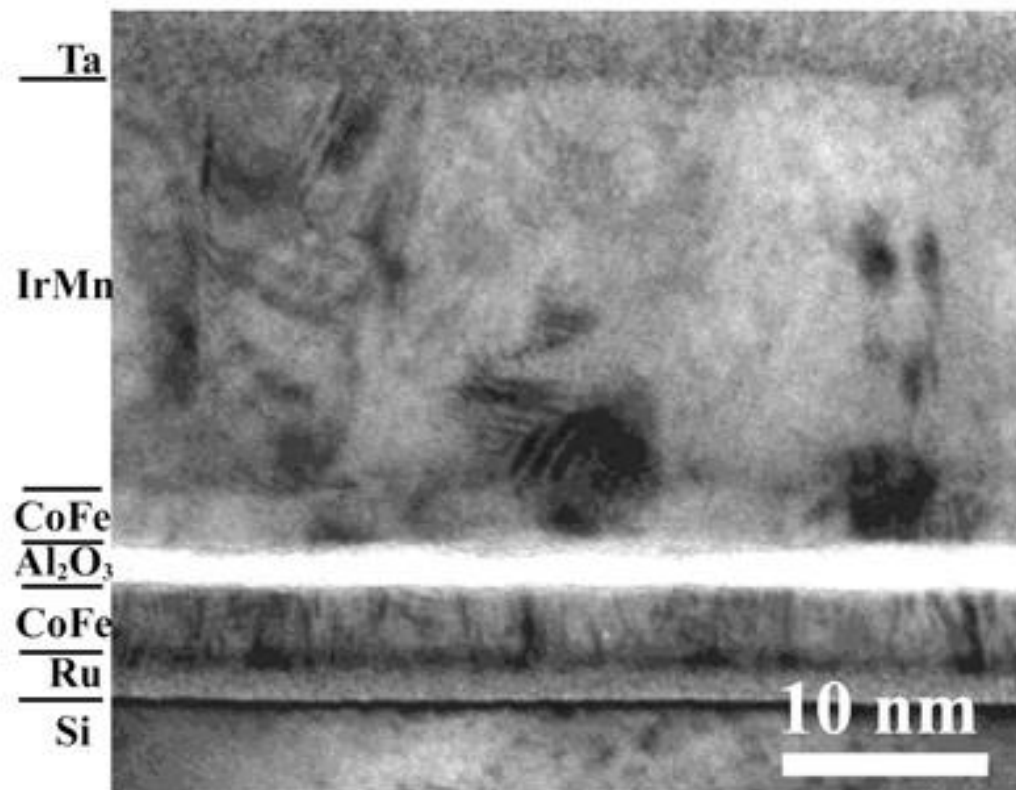
$$r = \frac{0.5 \lambda}{NA} = \frac{0.5 \lambda}{n \sin(\theta)}$$

while the Rayleigh criterion defines the resolution mathematically as:

$$r = \frac{0.61 \lambda}{NA} = \frac{0.61 \lambda}{n \sin(\theta)}$$

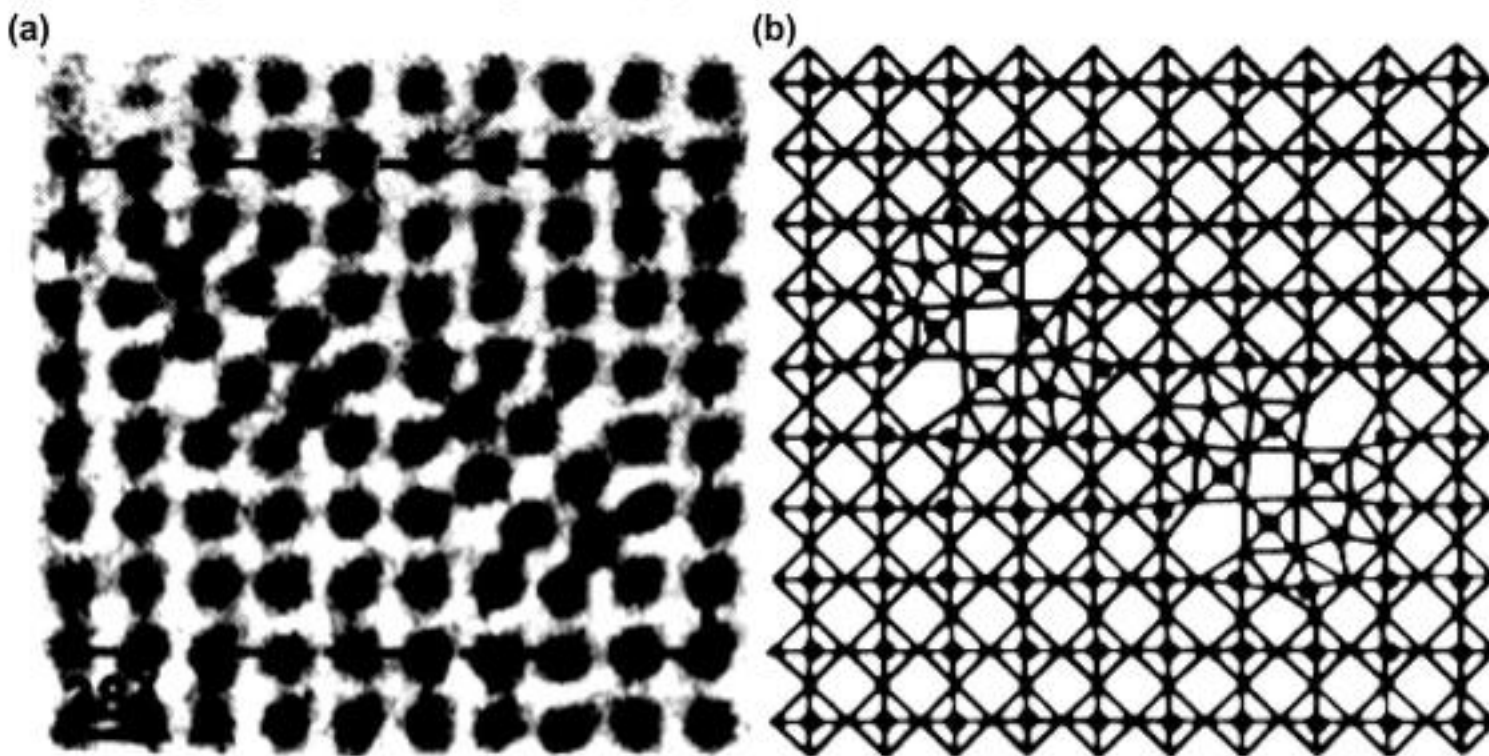


**Fig. 1.1** Atomic-resolution electron micrograph of Al  $6^\circ$  [001] symmetric tilt grain boundary with misfit accommodation by  $[110]/2$  edge dislocations (arrowed). Each black spot corresponds to projection of individual Al atomic column.



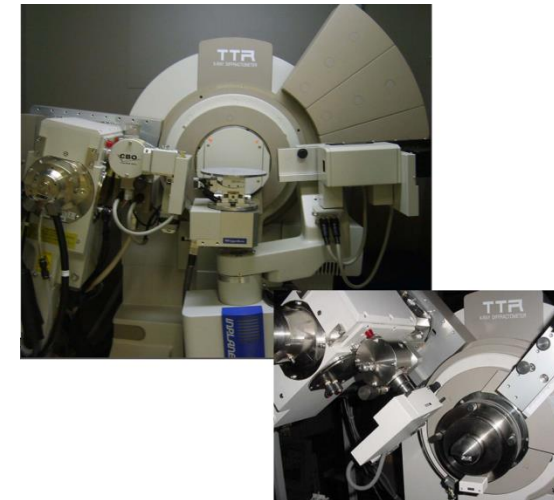
**Fig. 1.2** Bright-field electron micrograph showing the cross-section of a typical magnetic tunneling transistor device structure with a Ru seed layer between the Si(001) collector substrate and the CoFe base layer (Reproduced from ref. [11](#)).





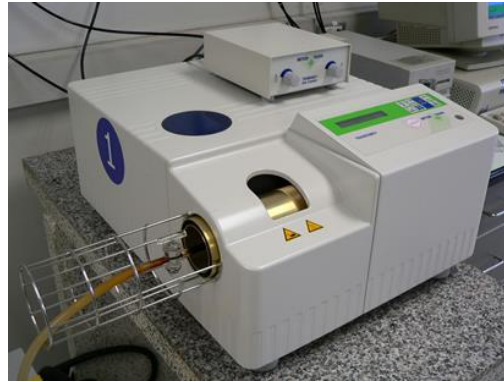
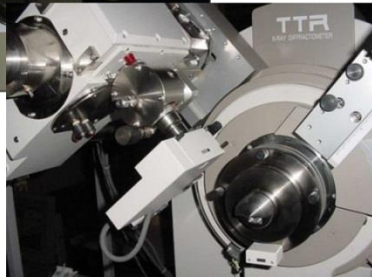
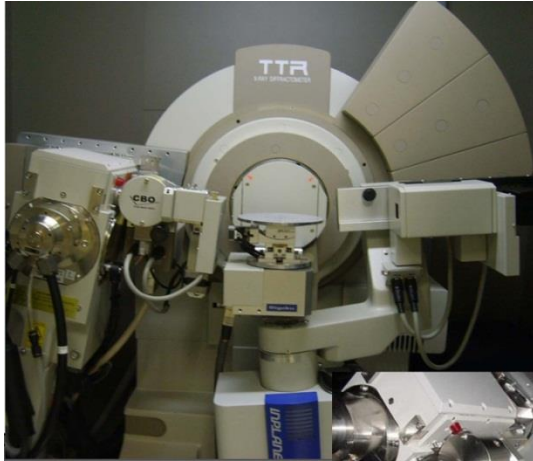
**Fig. 1.6** (a) Atomic-resolution electron micrograph of non-stoichiometric  $(\text{W}, \text{Nb})\text{O}_{2.93}$  showing pairs of pentagonal bipyramidal columnar defects. (b) Corresponding structural model. Occupied tunnel sites are located by direct visual inspection (Reproduced from ref. [42](#)).

# หน่วยวิเคราะห์ลักษณะเฉพาะของวัสดุ





# Physical Characterization Lab: PhCL

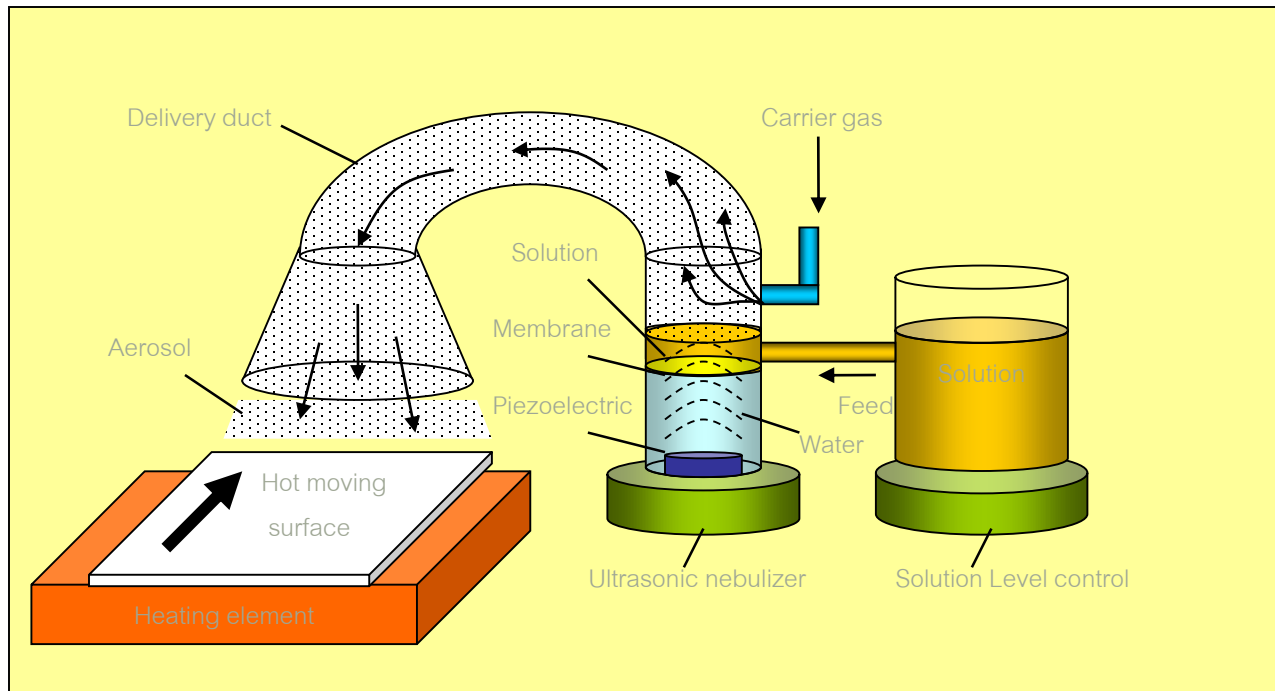




A graphic of three overlapping circles in shades of green, arranged vertically to resemble a thought bubble. The top circle is the largest and lightest, with two smaller, darker circles below it.

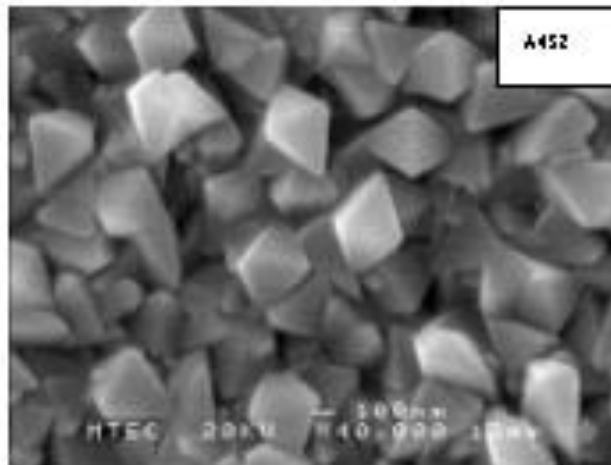
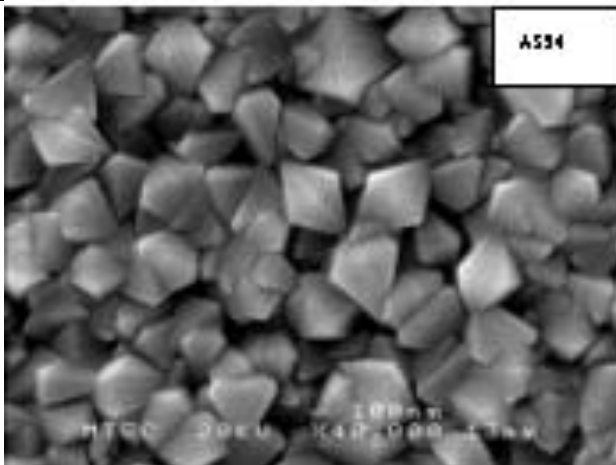
# Research Examples

# SnO<sub>2</sub>:F deposition



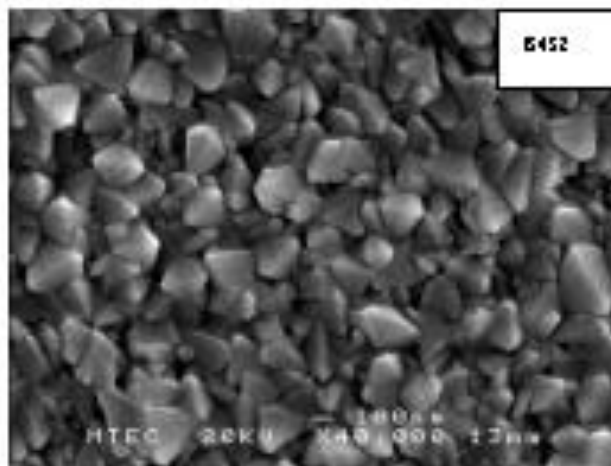
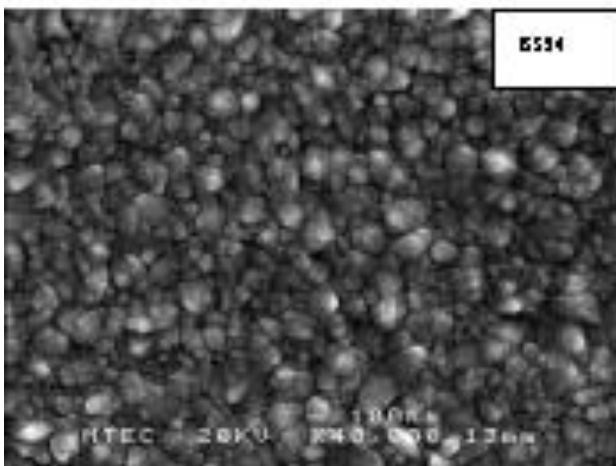
**Schematic diagram of pyrosol deposition  
("pyrosol" = pyrolysis of aerosol)**

394 °C,  
condition A



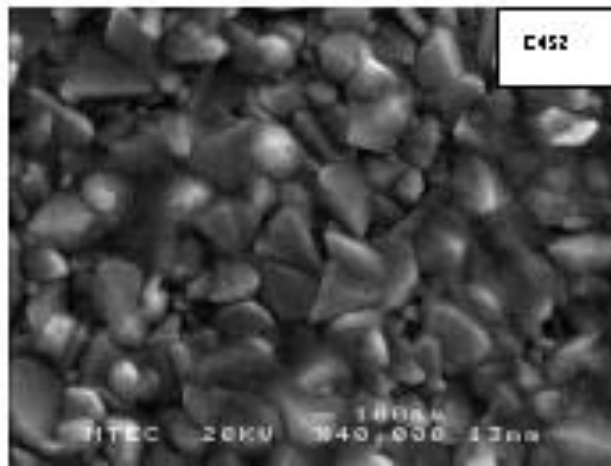
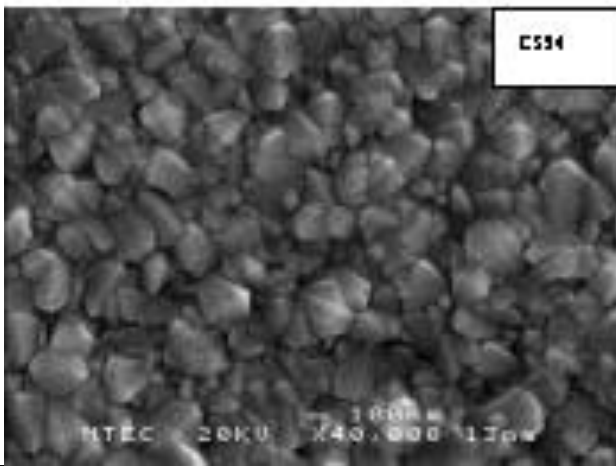
432 °C,  
condition A

394 °C,  
condition B

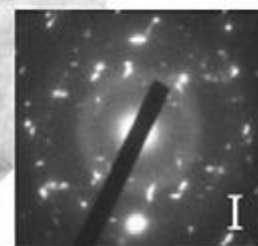
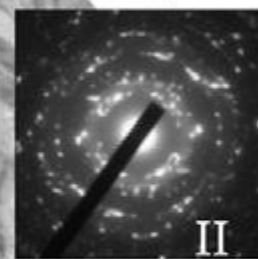
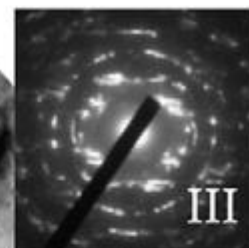
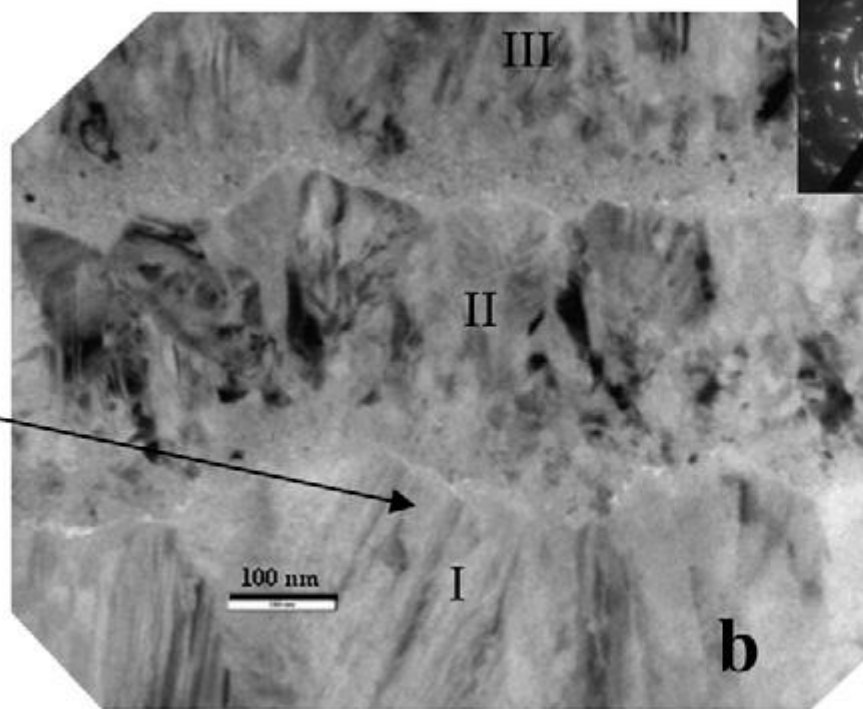
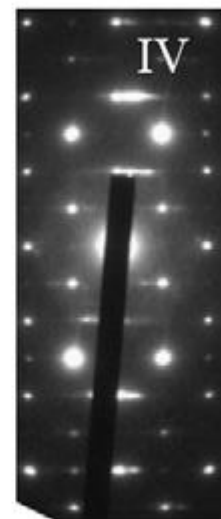
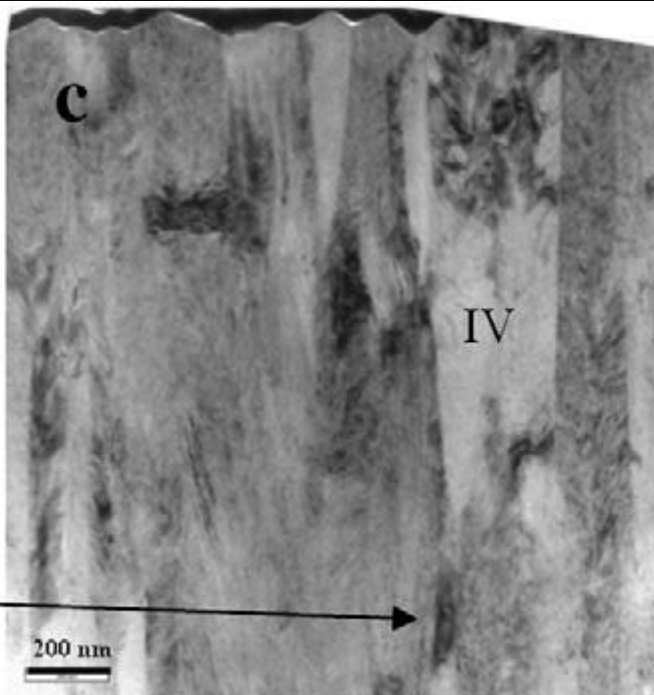


432 °C,  
condition B

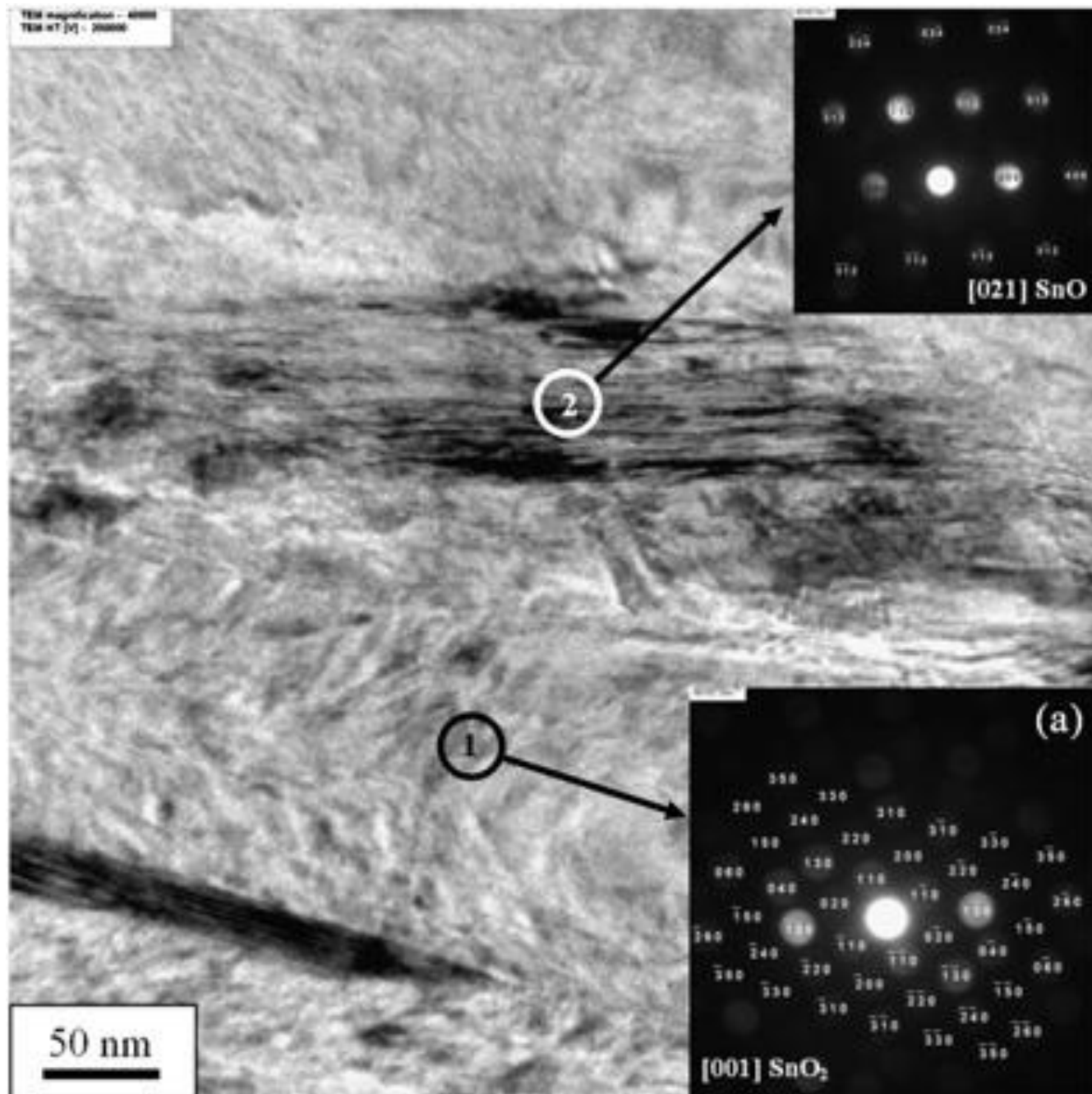
394 °C,  
condition C



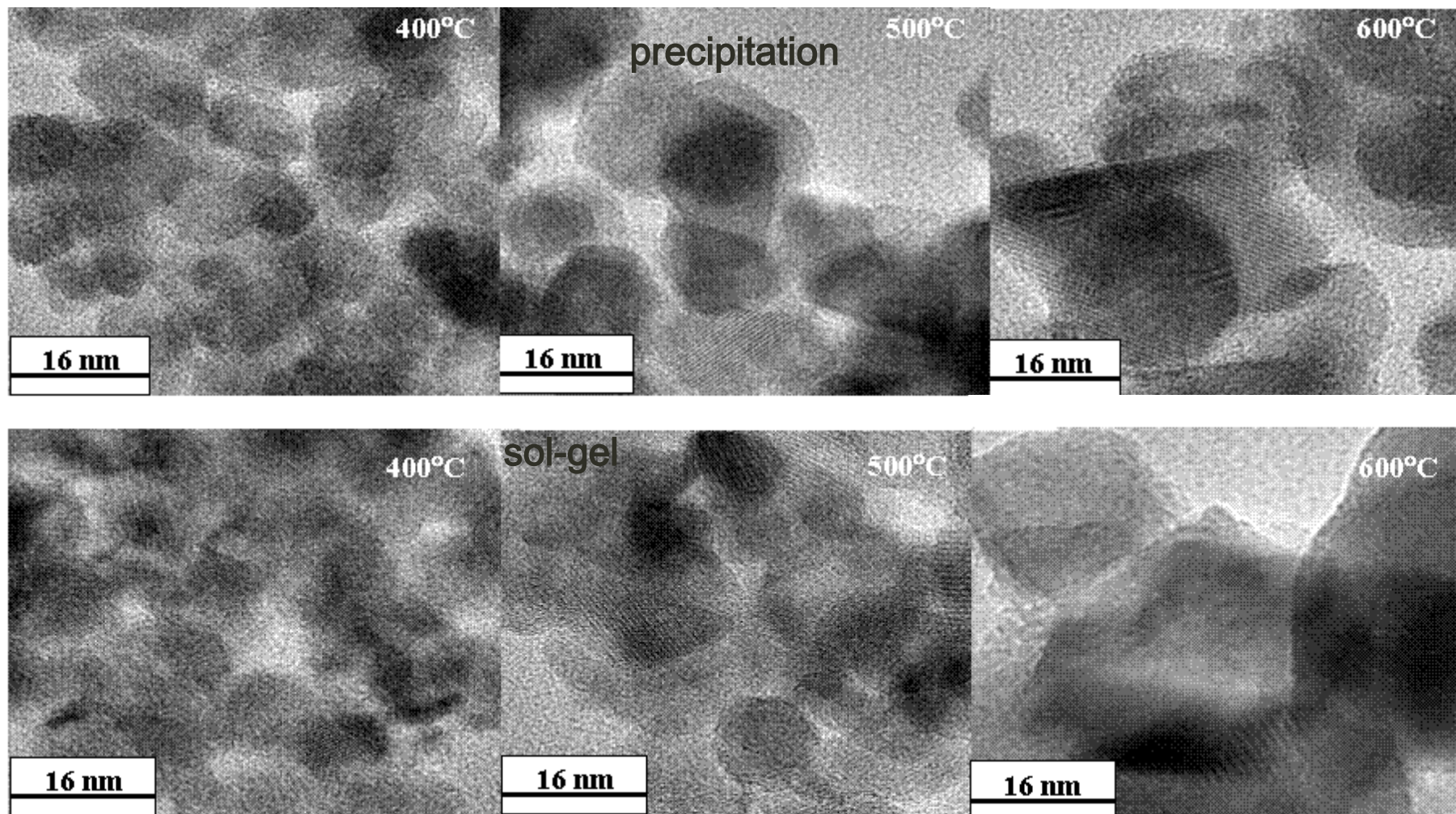
432 °C,  
condition C





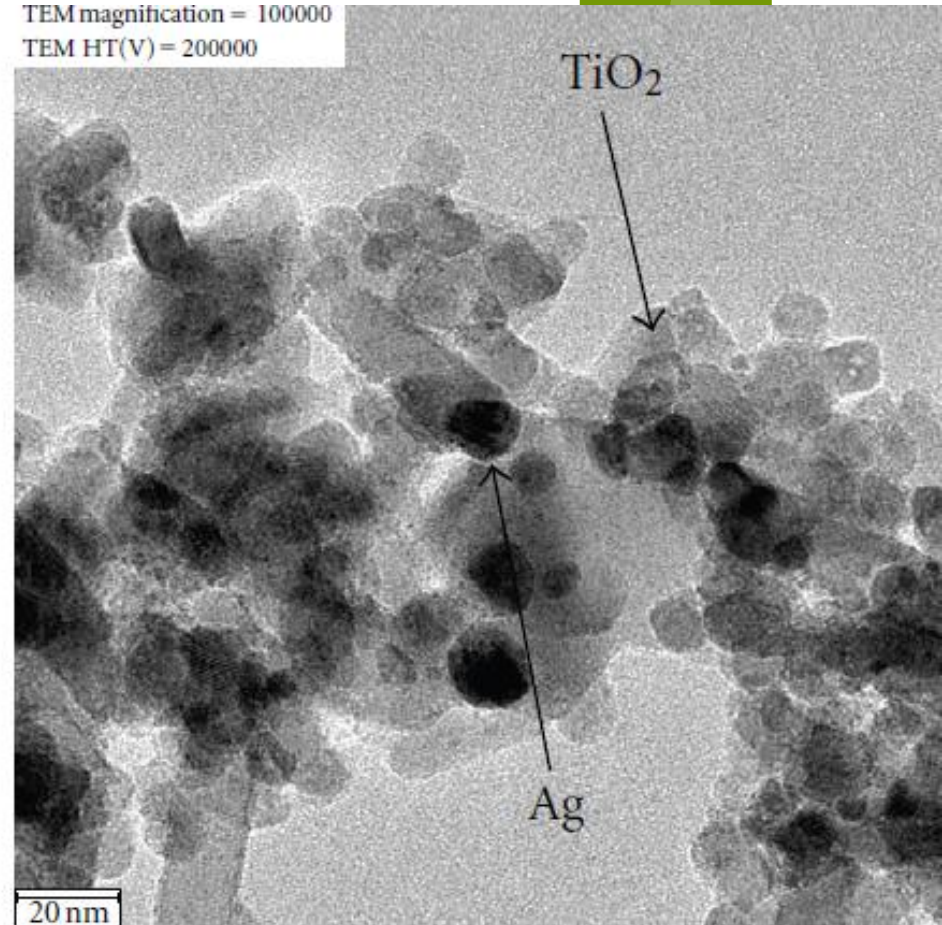
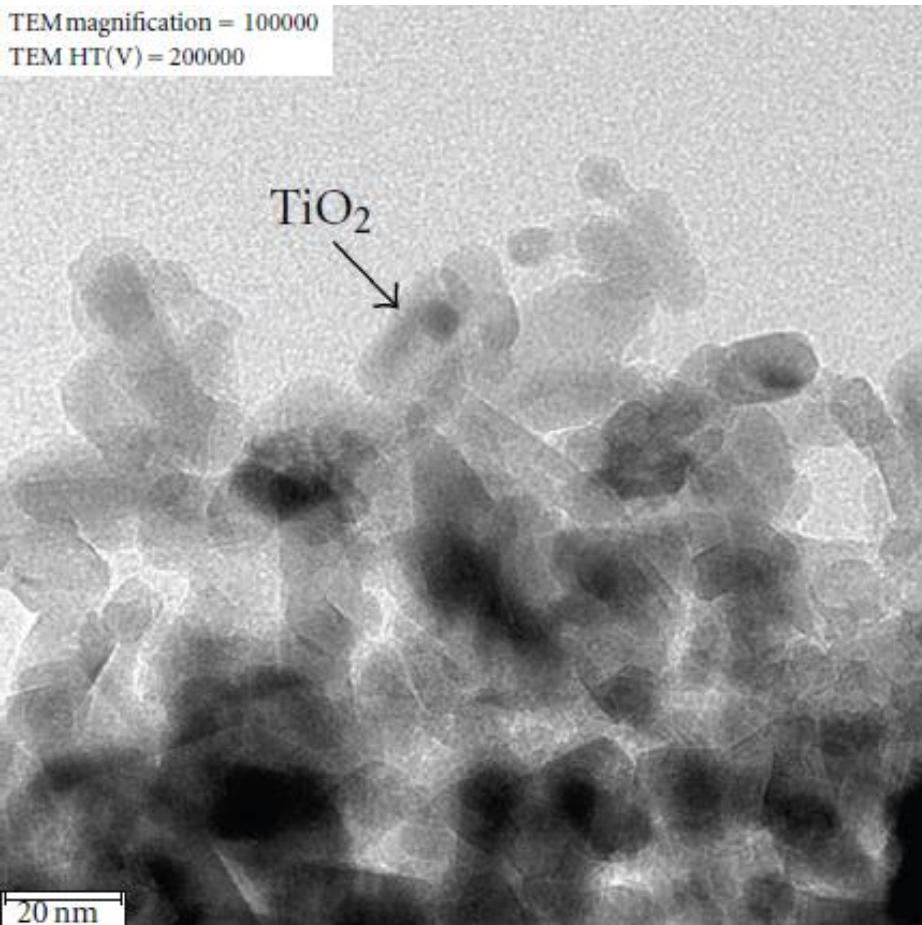


# TiO<sub>2</sub> nanoparticles (precipitation vs sol-gel)





# TiO<sub>2</sub> & Ag nanoparticles



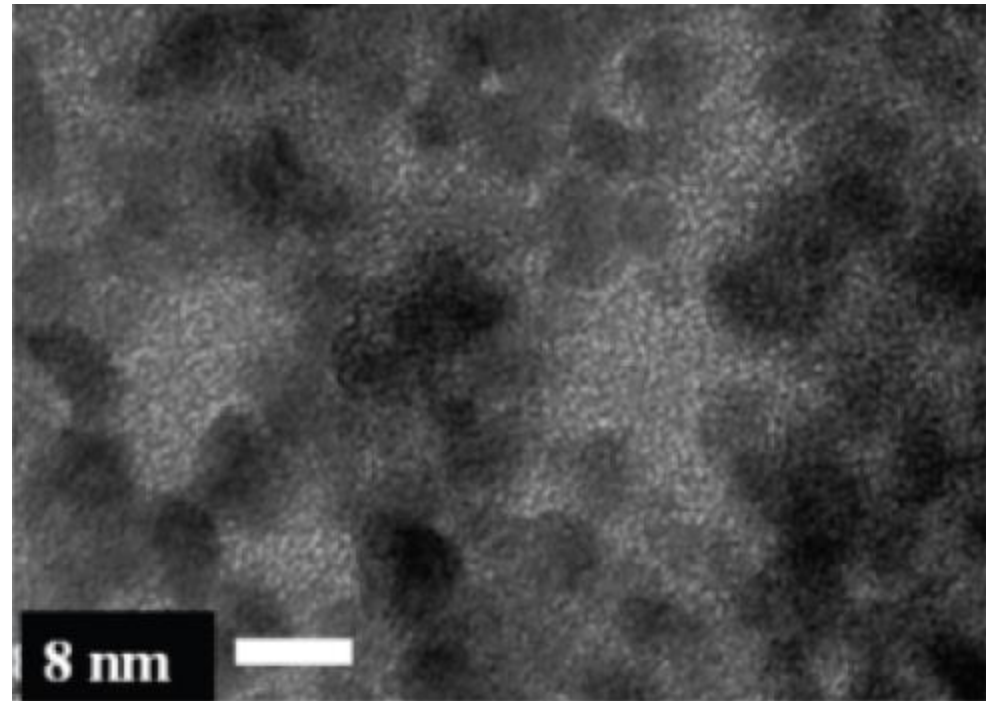
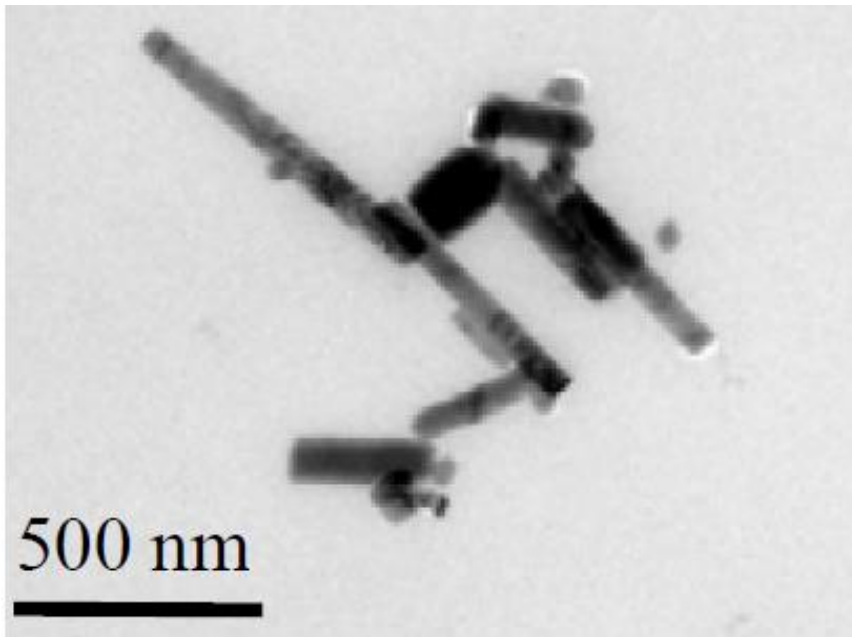
TEM micrographs of the TiO<sub>2</sub> nanotubes (a) before and (b) after immersion in the AgNO<sub>3</sub> solution with UV exposure for 120 minutes.

# ZnO nanoparticles (solvothermal vs precipitation)



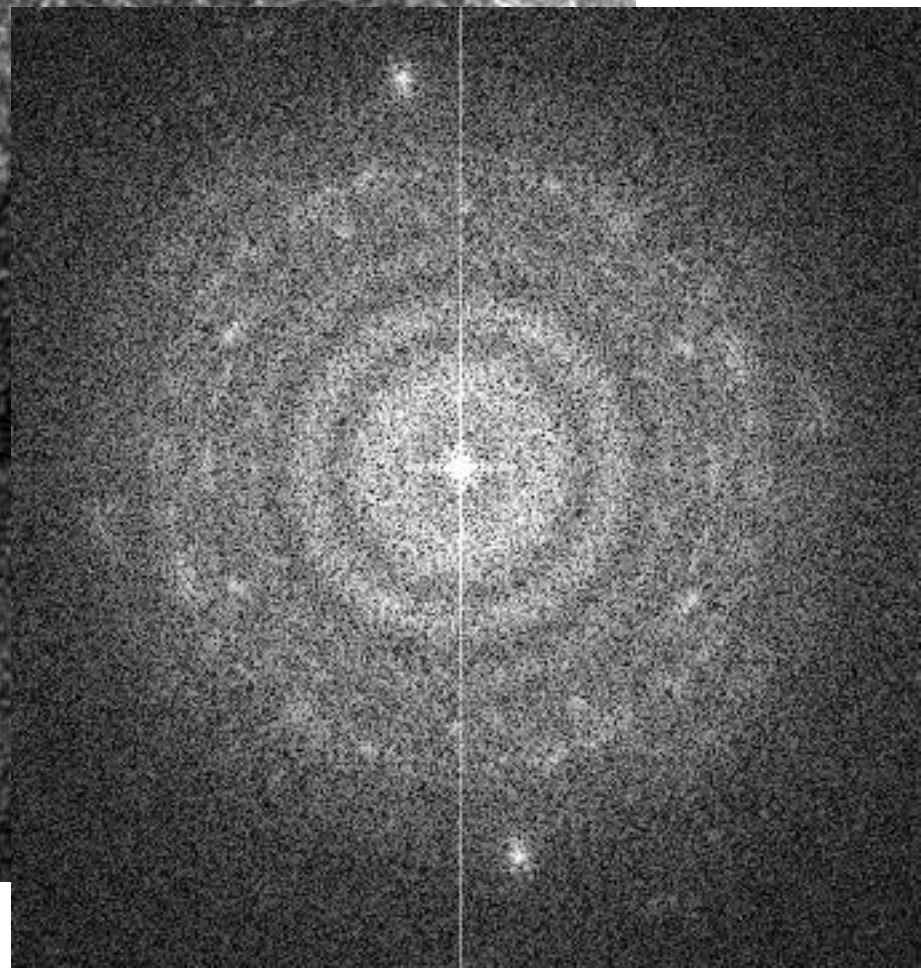
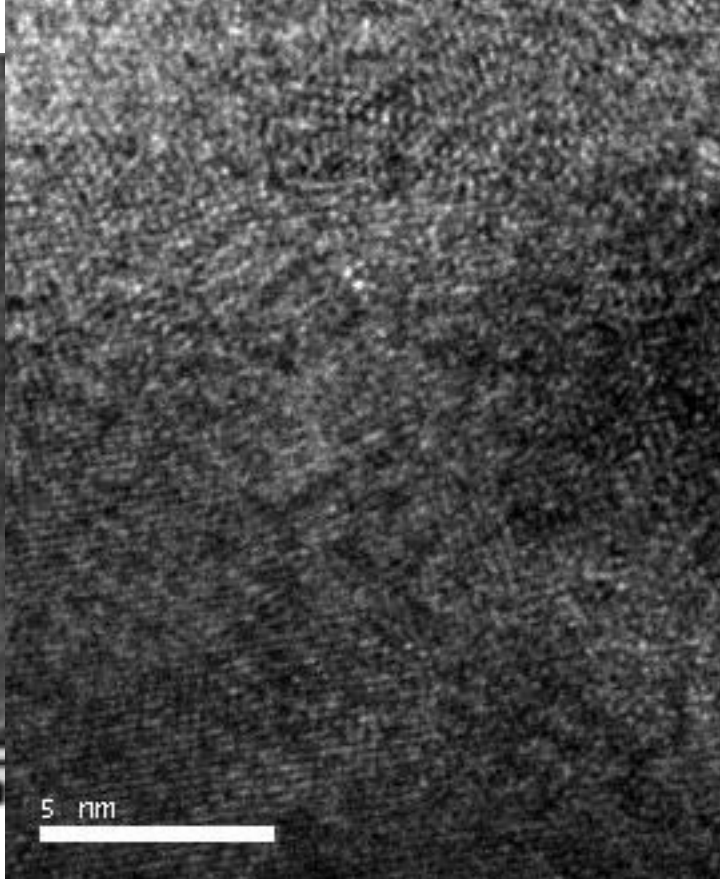
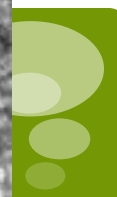
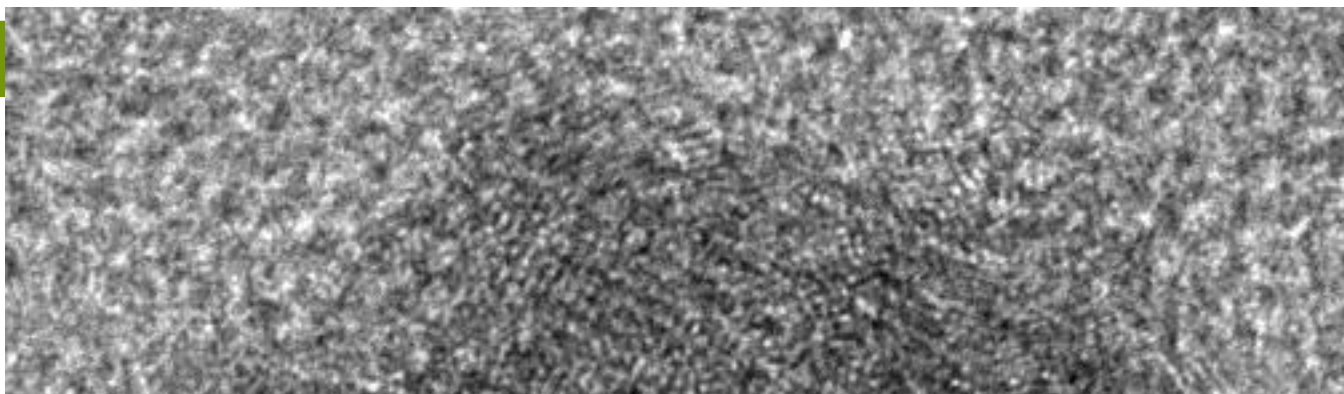
- solvothermal
- nanorods

- Precipitation
- spheres



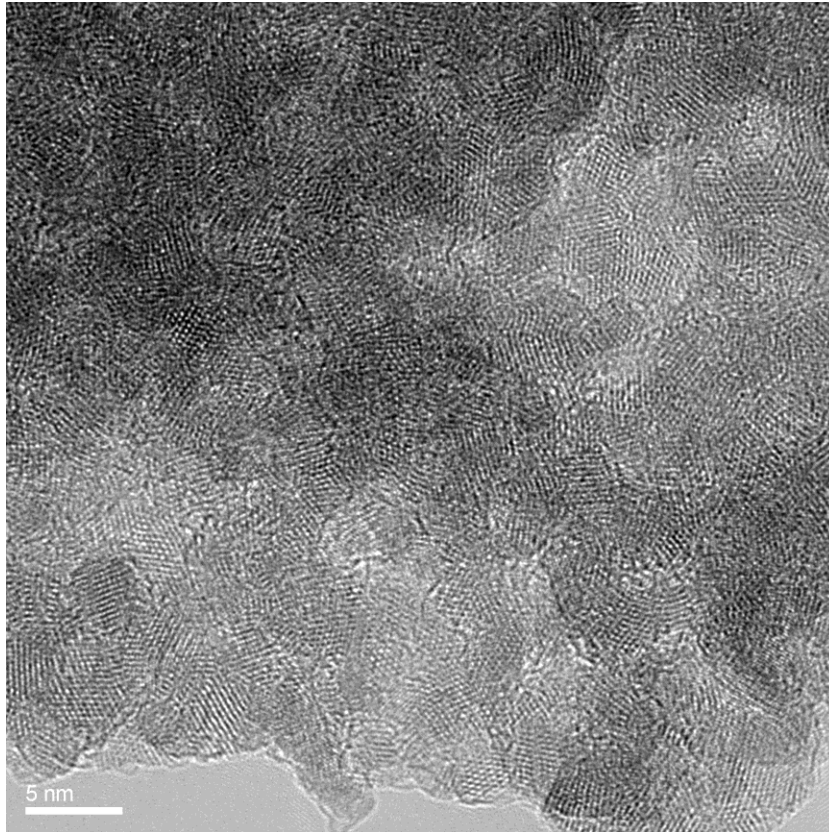


HRI





# HREM images of ZnS:Mn<sup>2+</sup>

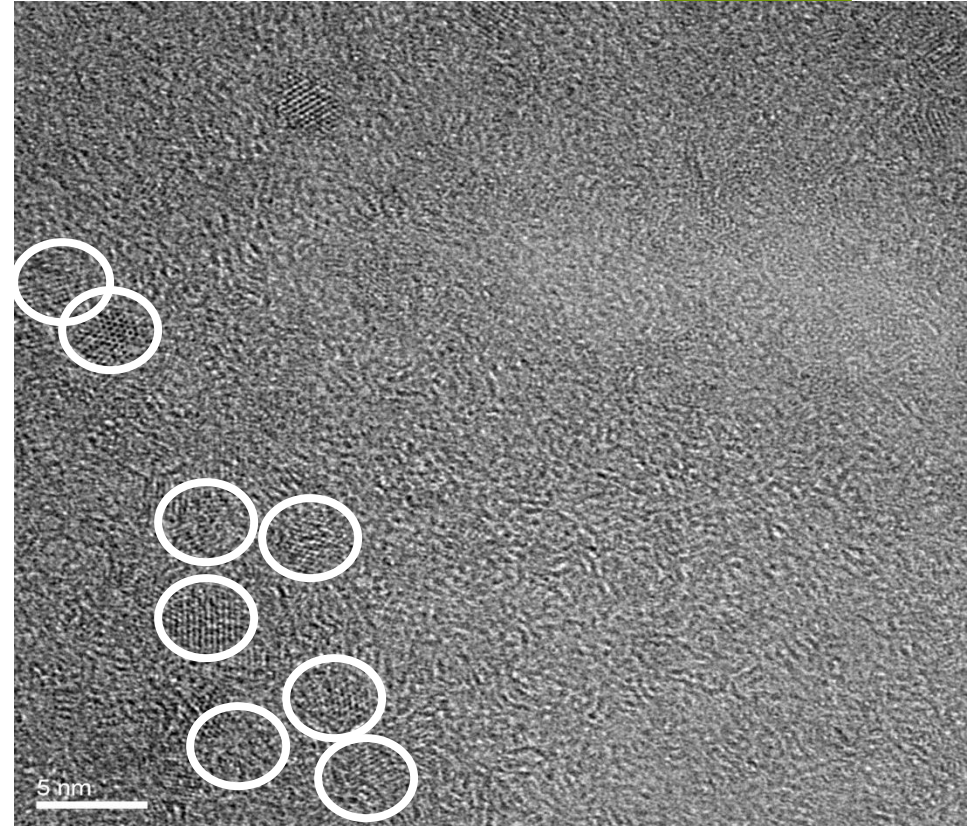


**Chitosan capped ZnS:Mn<sup>2+</sup>**

High concentration of Polycrystalline agglomerates of 3-5 nm crystallites

Average crystallite size = 2.54 nm

Crystallite density = 80,971  $\mu\text{m}^2$ .



**PVA capped ZnS:Mn<sup>2+</sup>**

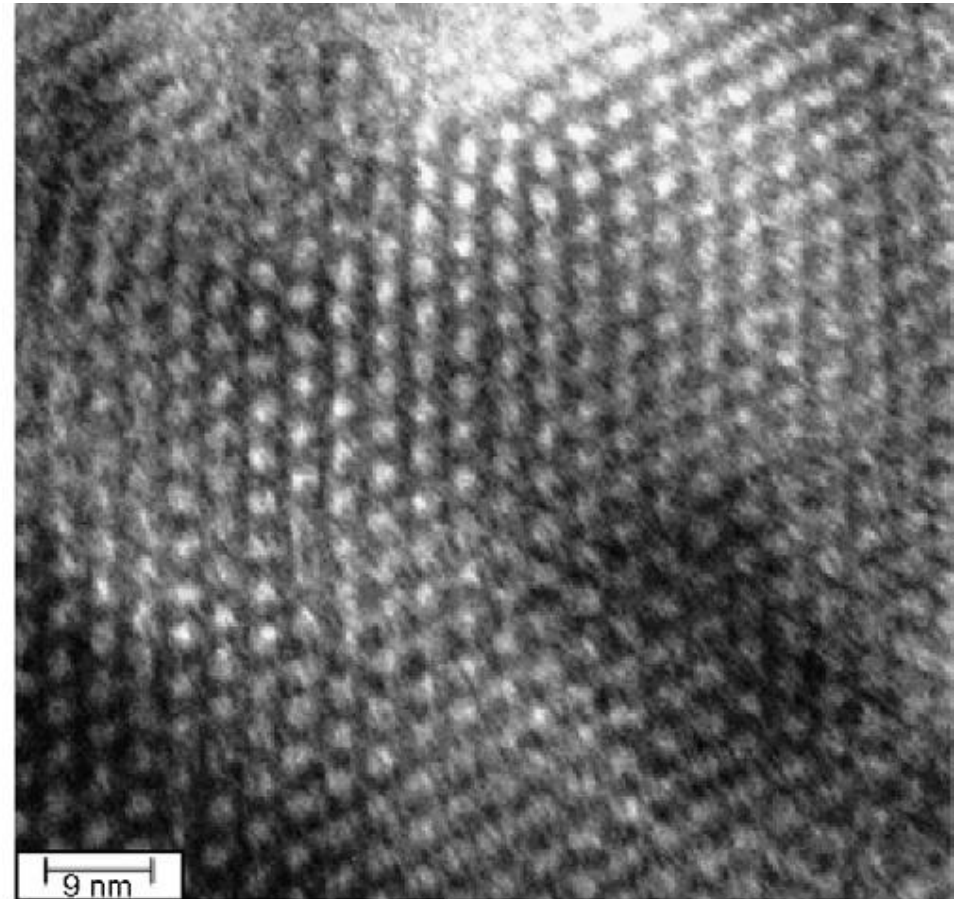
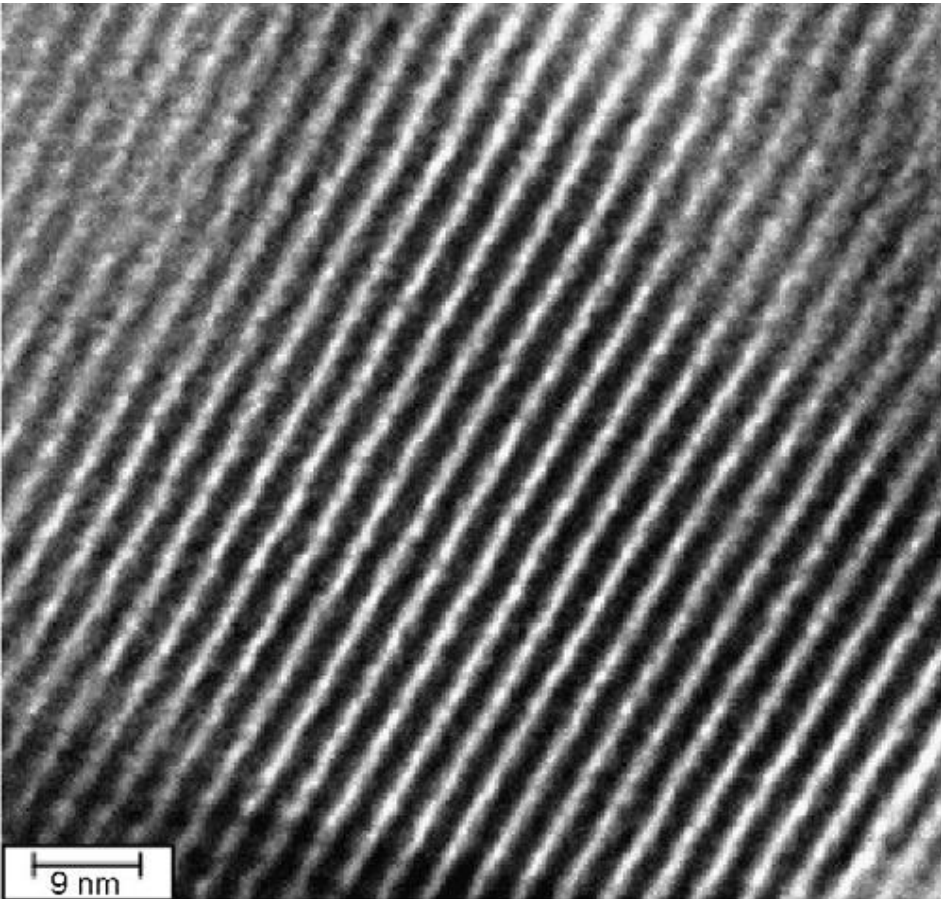
Rare Polycrystalline agglomerates of 3-5 nm crystallites (encircled for visual effects)

Average crystallite size = 2.56 nm

Crystal density = 19,856  $\mu\text{m}^2$

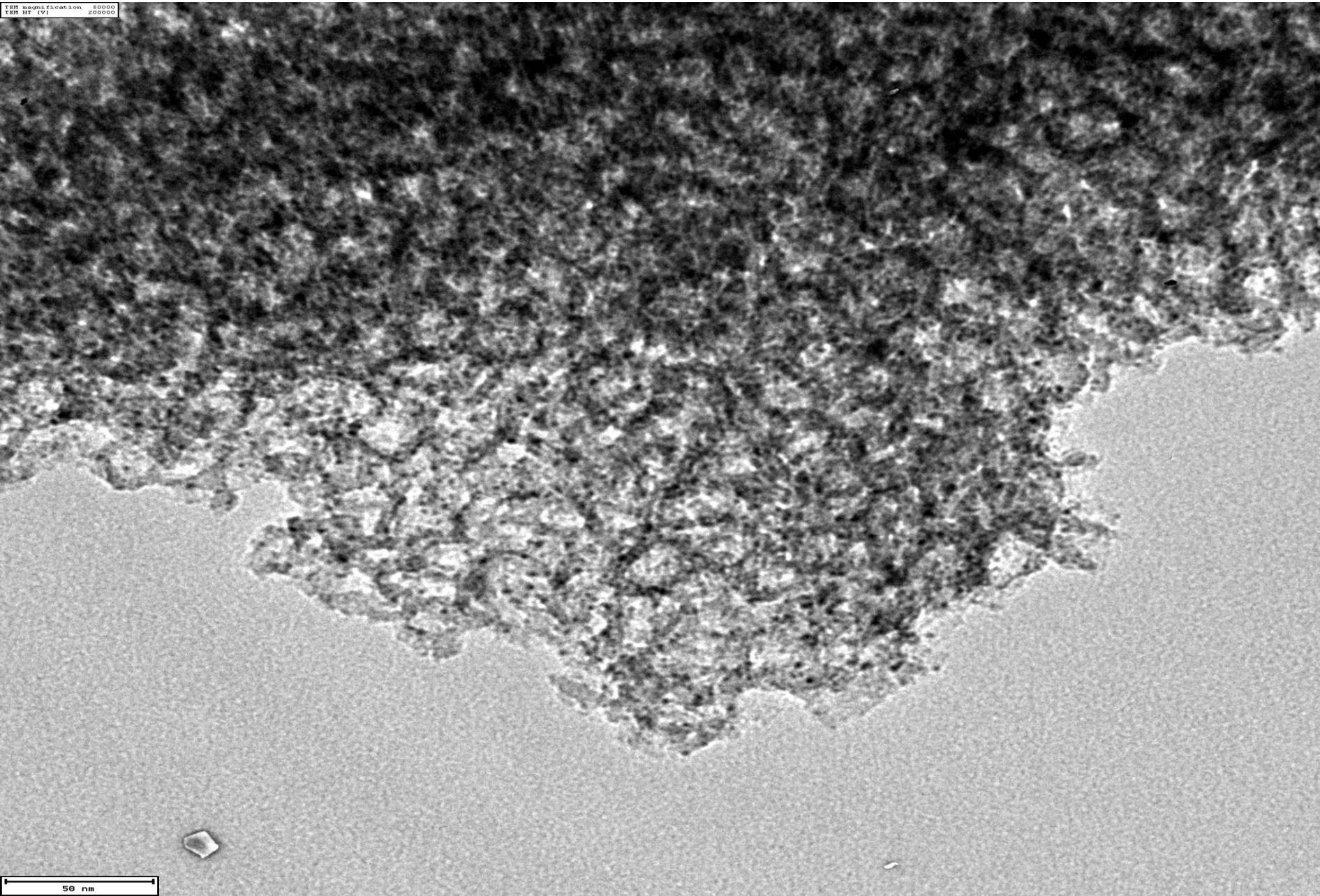


# TEM images of mesoporous silicas



**perpendicular (left) and parallel (right) to the pores**

TEM MAGNIFICATION 50000  
TEM HT (V) 200000





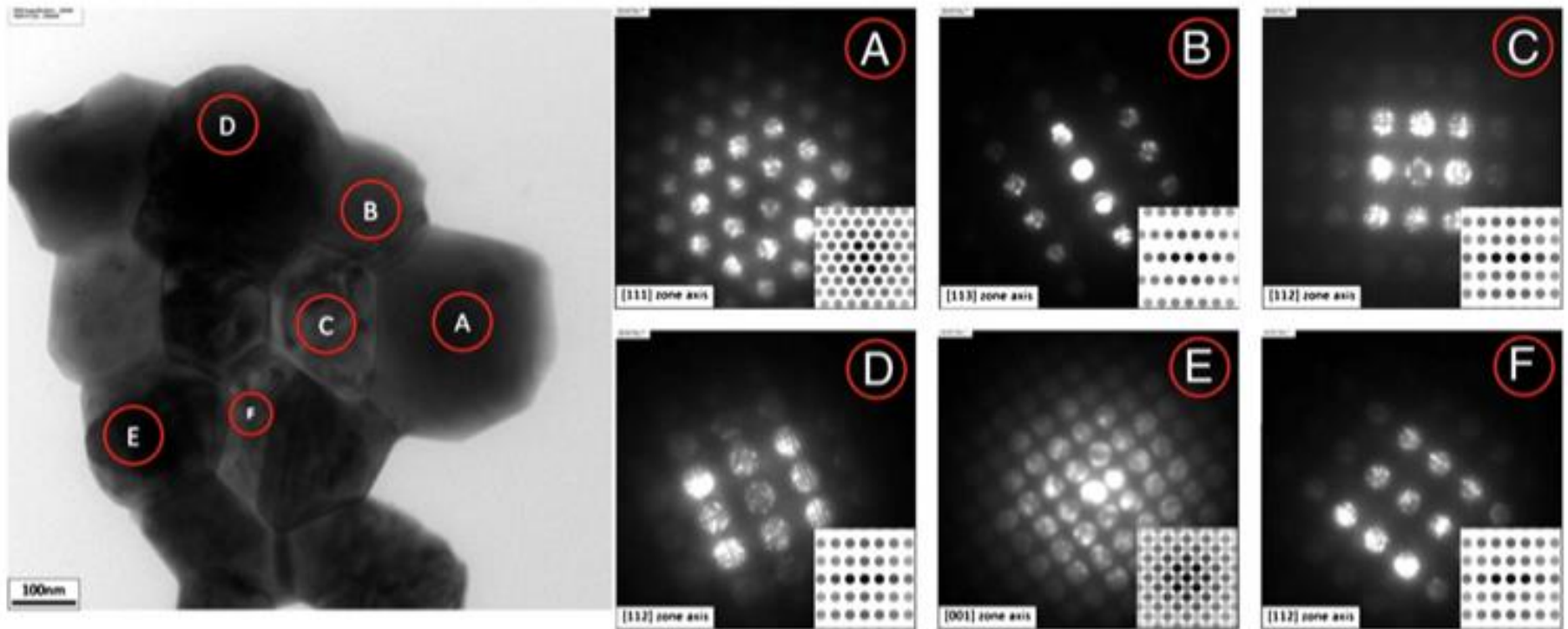
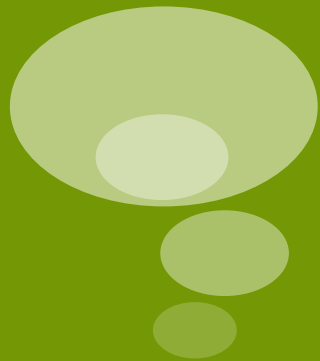


Fig. 4. CBED patterns of  $\text{Ba}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$  obtained from 6 grains (A-F).

# Conclusion



- Advanced Microscopy is not difficult but
  - Equipment expensive
  - Maintenance expensive
  - Equipment operators must be skillful
  
- But it's conventional
  
- In order to characterize advanced nanomaterials
  - Advanced microscopy
  - Advanced spectroscopy
  - More expensive equipment
  - More skillful operators



Thank you

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