# Advanced electron microscopy techniques for materials science

Alexander Neirinckx

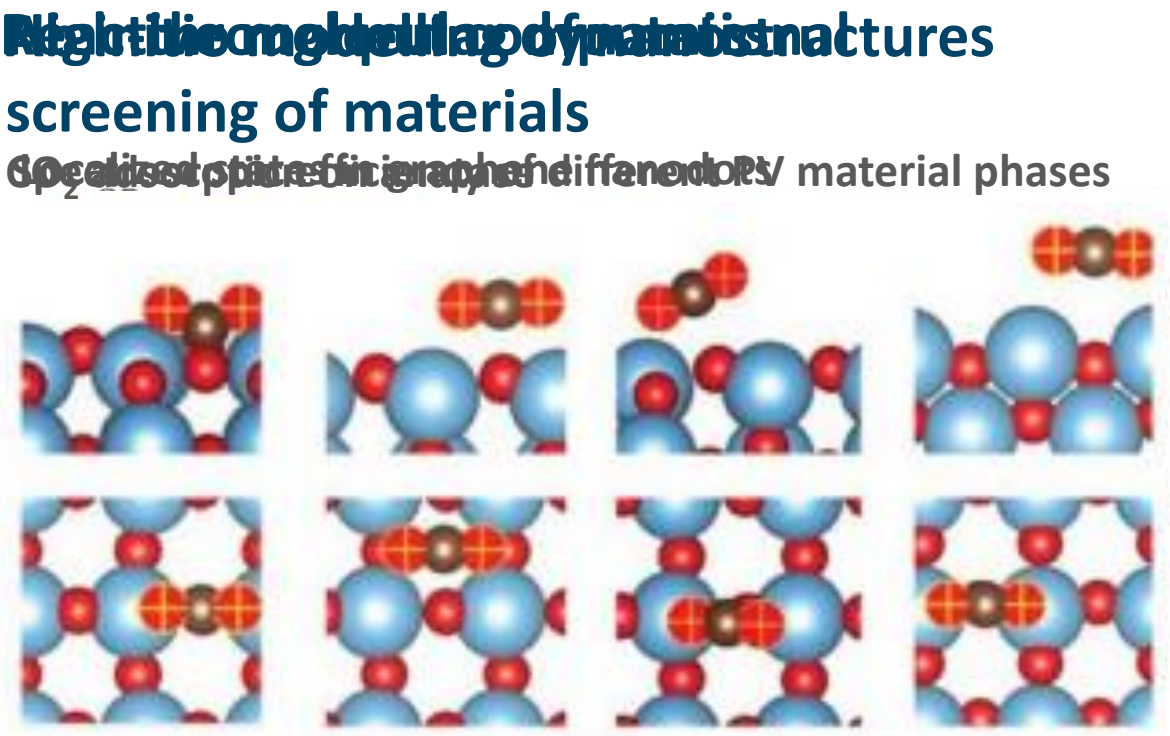
University of Antwerp

University of Antwerp NANOcenter IOF consortium | Electron Microscopy for Materials Science | CMT Condensed Matter Theory | PLASMANT Plasma, Laser Ablation and Surface Modelling Antwerp

Universiteit Antwerpen

# NANOcenter consortium

- Expertise in nanomaterials at the University of Antwerp.
- Three groups: EMAT, CMT and PLASMANT (~110 researchers)
- Advanced characterization & modelling of growth/composition of (nano)structures and their properties



# EMAT in numbers

Electron Microscopy for Materials Science
University of Antwerp

**8 Professors**
**40 Researchers**
**5 Tech staff**

**~900** publications (since **2010**), including:
**7 Nature Materials**
**2 Nature**
**117** papers (impact factor 11.31)

**6 Transmission Electron Microscopes:**
**2 Scanning Electron Microscopes**
**1 Focused Ion Beam SEM**
**1 X-ray diffractometer**

# Advanced microscopy techniques

## 3D reconstruction

- Electron tomography
- Spectral tomography

## In situ measurements

- Nano-tensile tests

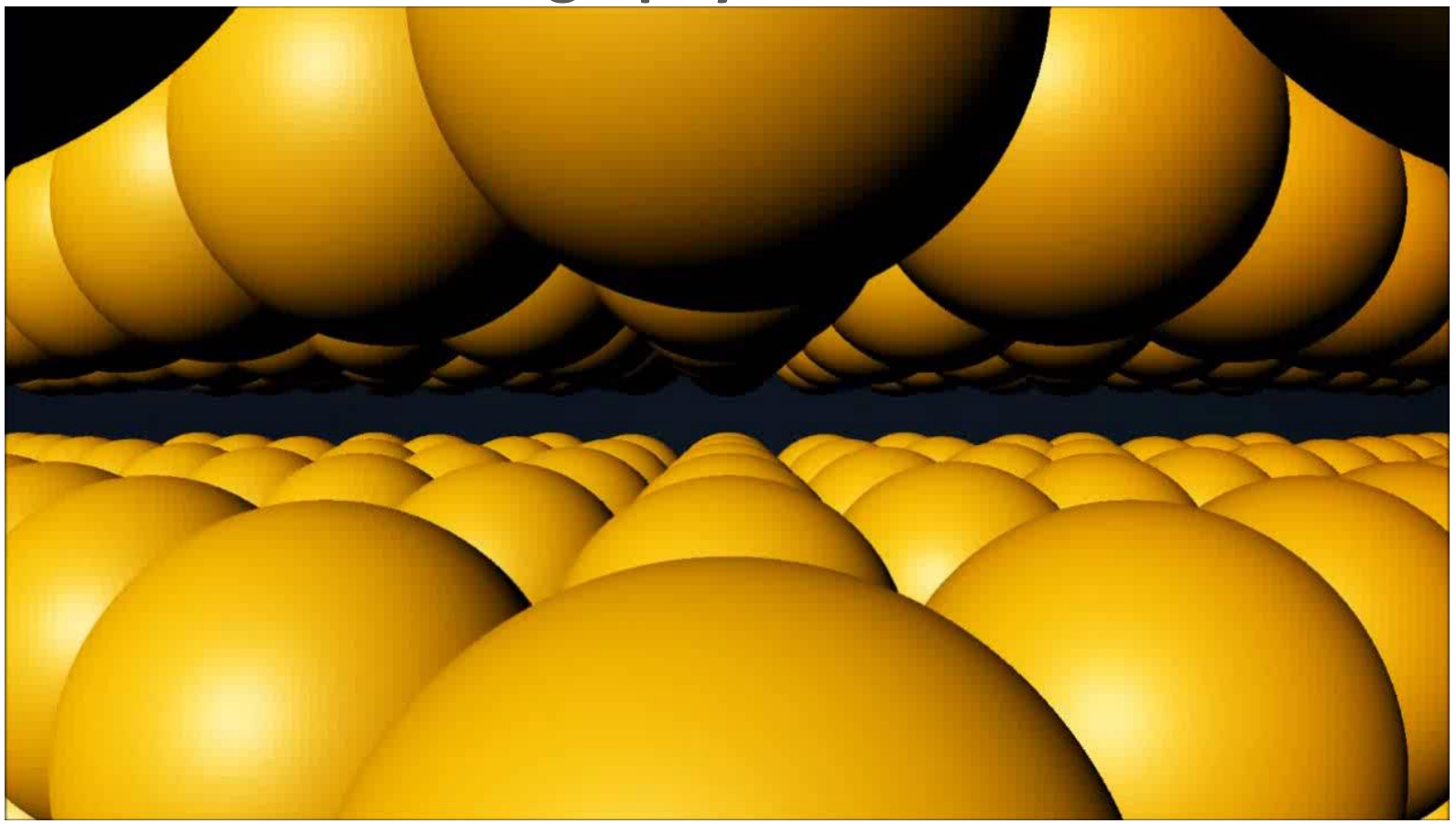
## Dealing with beam sensitive materials

- Compressed sensing

## Future outlook

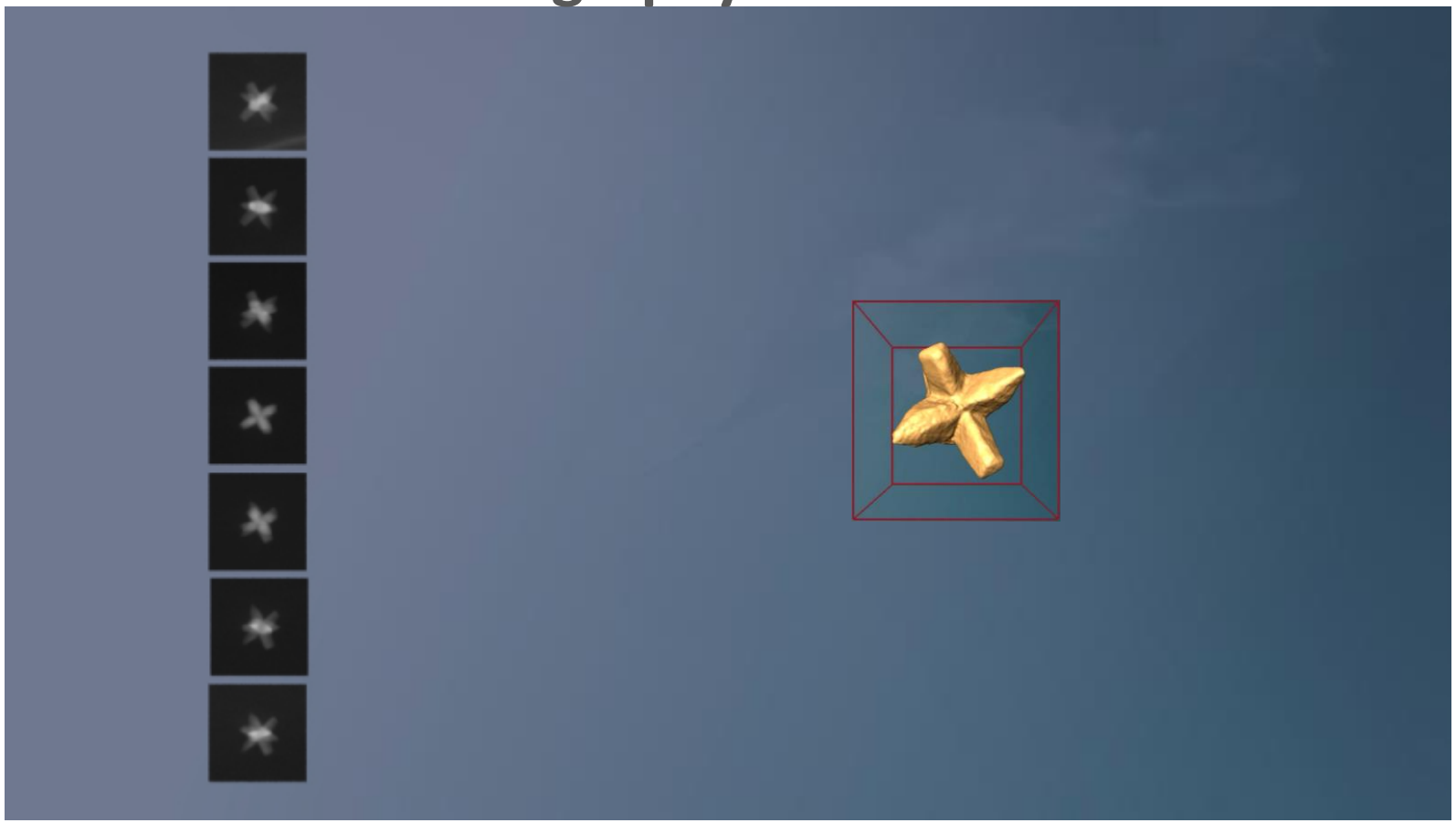
# 3D reconstruction

## What is electron tomography?



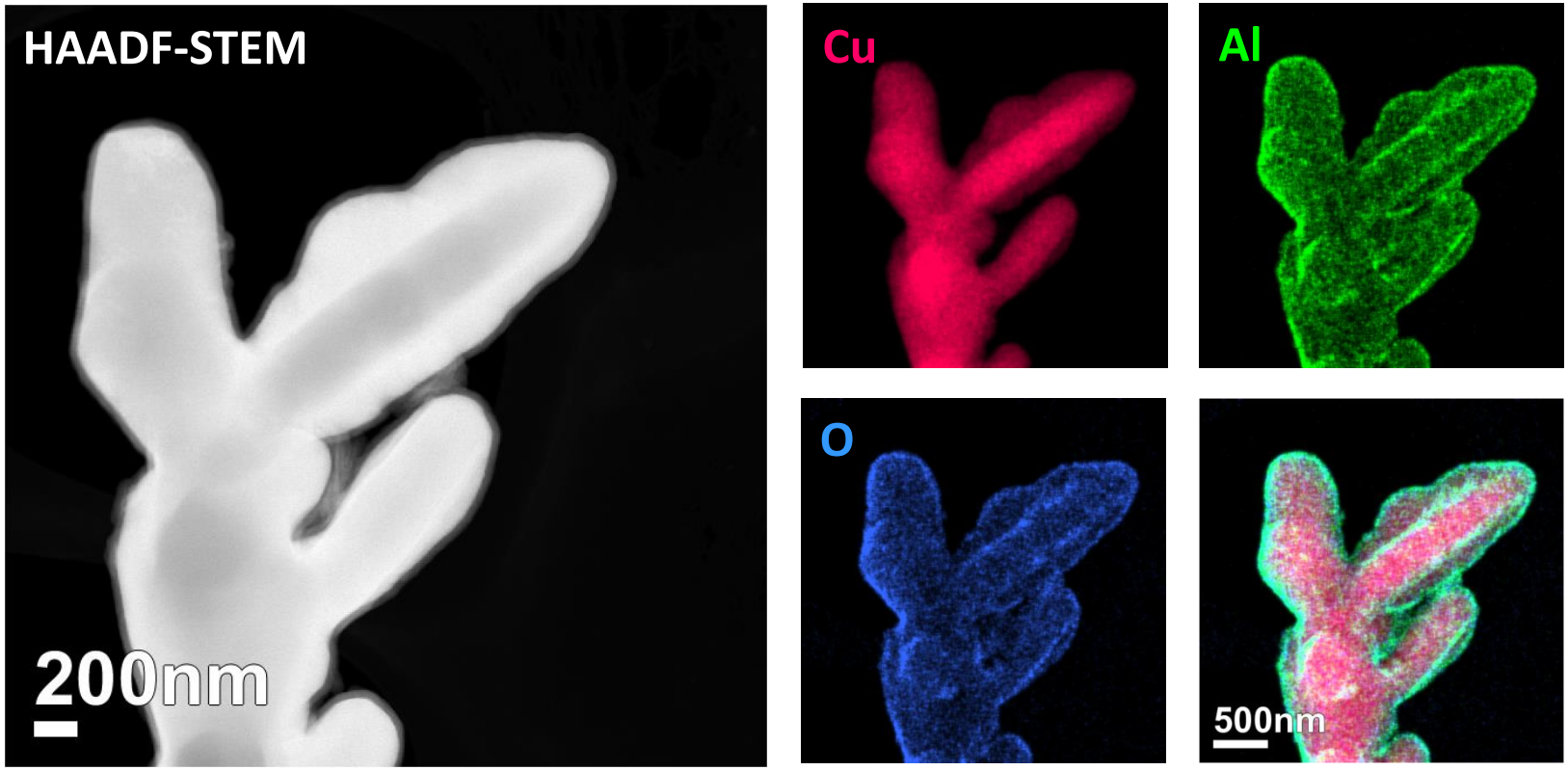
# 3D reconstruction

## What is electron tomography?



# Electron tomography

## Investigating coating uniformity




Atomic Layer Deposition (ALD) coated Cu powder

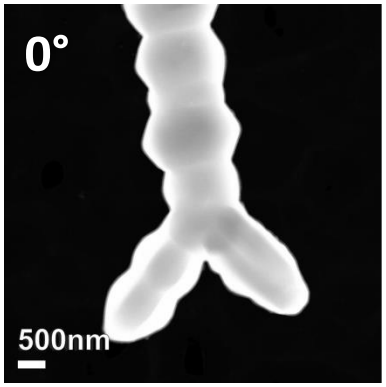
➔ EDX-maps and HAADF images show presence of Al-coating...

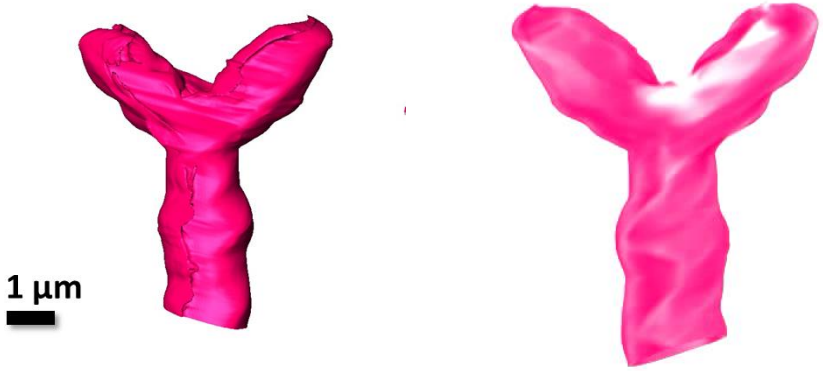
But is it uniform?

*Samples courtesy of Prof. C. Detavernier, Universiteit Gent*

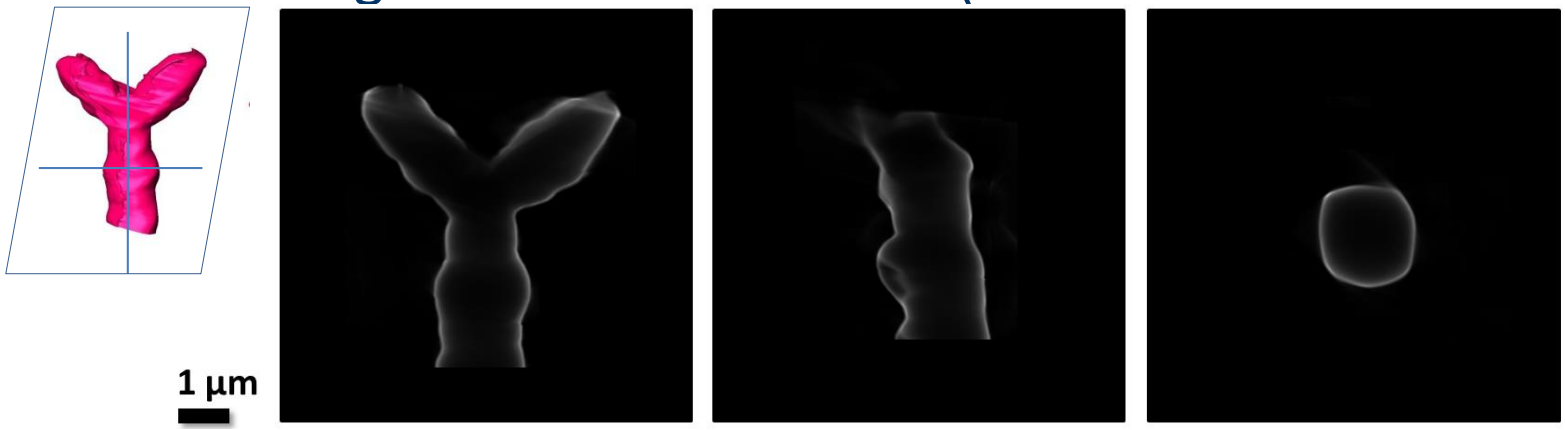
# Electron tomography

## Investigating coating uniformity



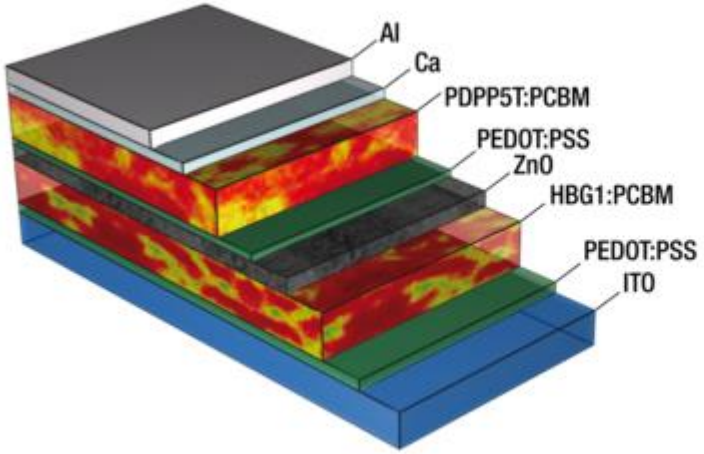

- HAADF-STEM images from -78° to +78° (2° steps). Reconstruction with SIRT algorithm.
- Slices through the 3D visualization (in different orientations):

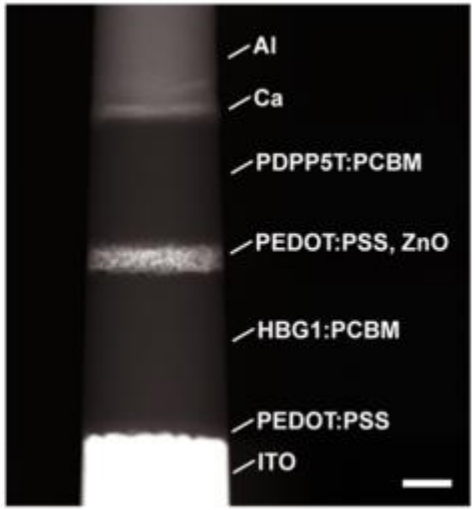


# Spectral tomography

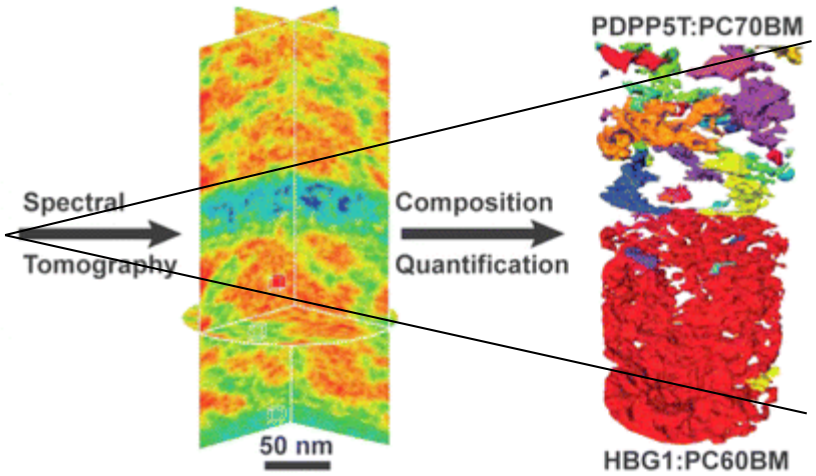
## Combination with Electron Energy Loss Spectroscopy

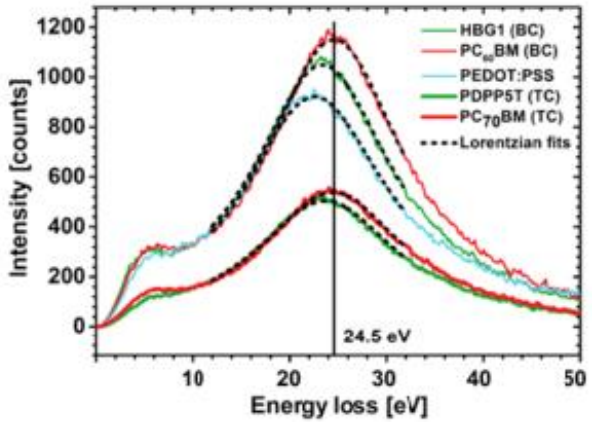
OPV solar cell




Preparation of FIB “needle” structure Identification of Low Loss spectrum

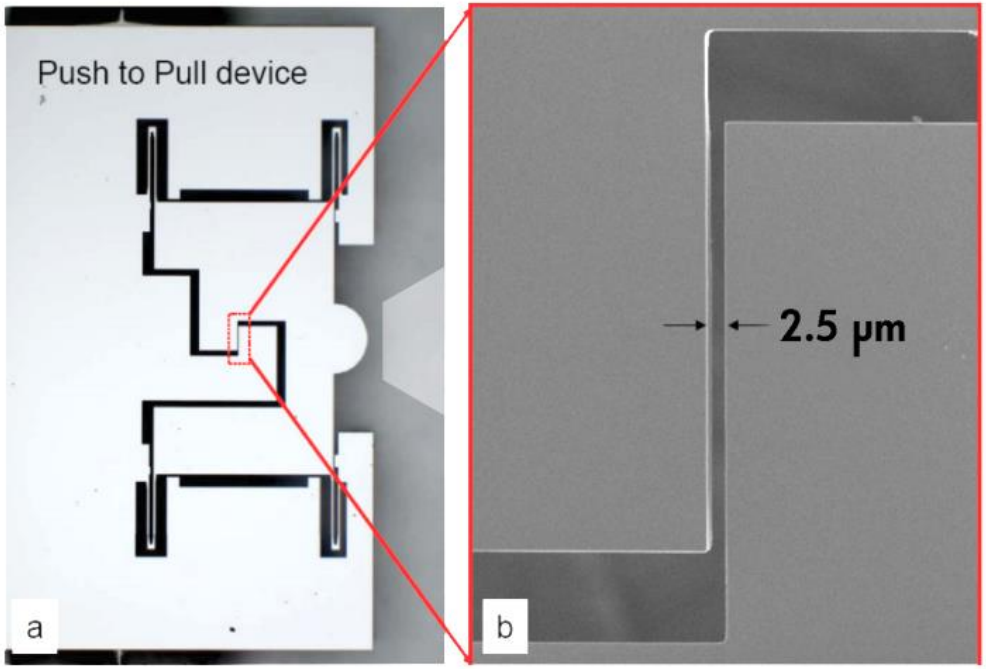



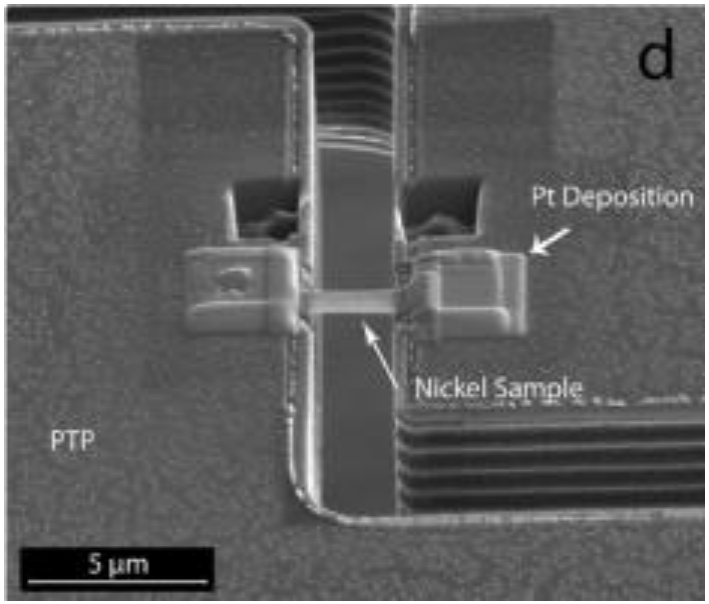

*Pfanmöller et al., Nano Lett. 15:6634-6642 (2015)*

# In situ TEM: nano tensile test

## Push to pull experiments

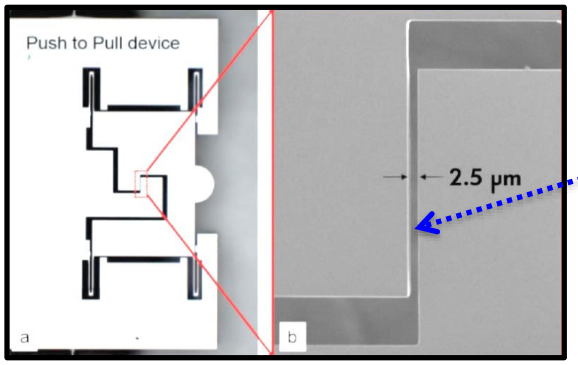

**Quantitative results**

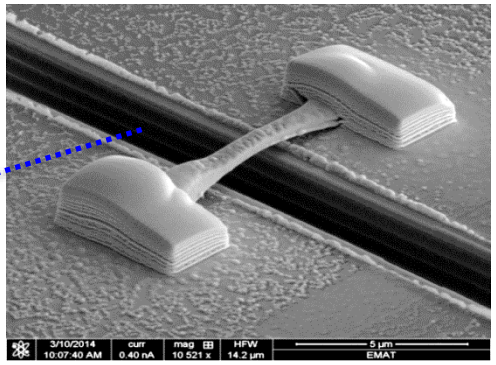


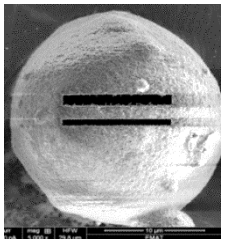



# In Situ TEM: nano tensile test

## Study of capsule shell

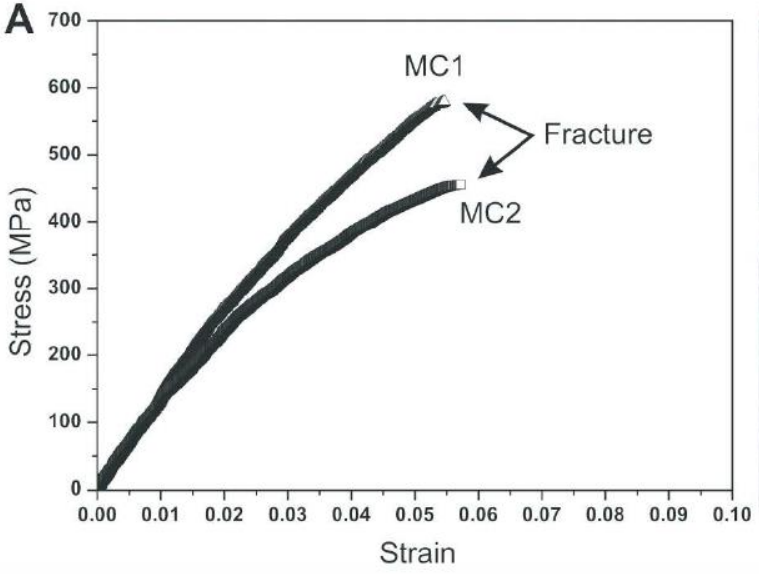


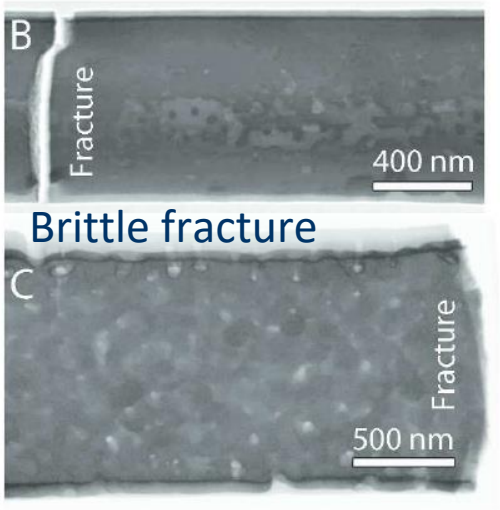





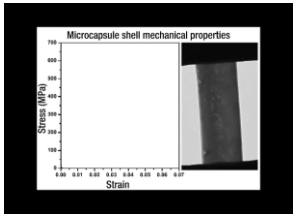
Using Push-to-Pull unit in PicoIndenter holder

## Stress-Strain curve of methylformalhyde microcapsule



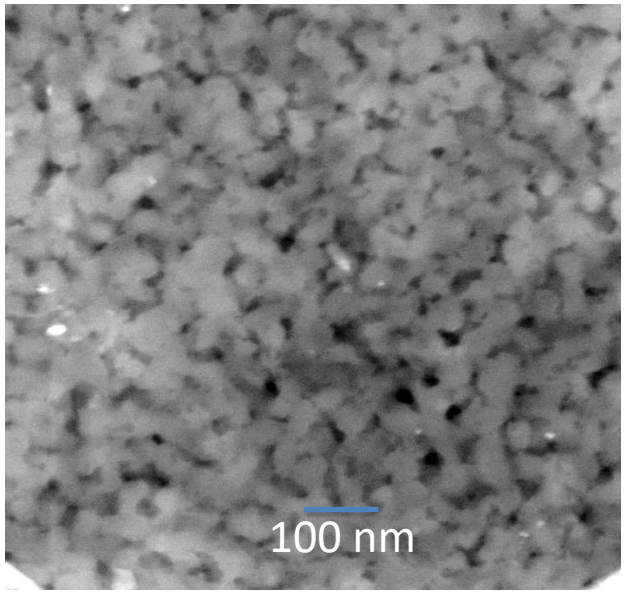




Brittle fracture



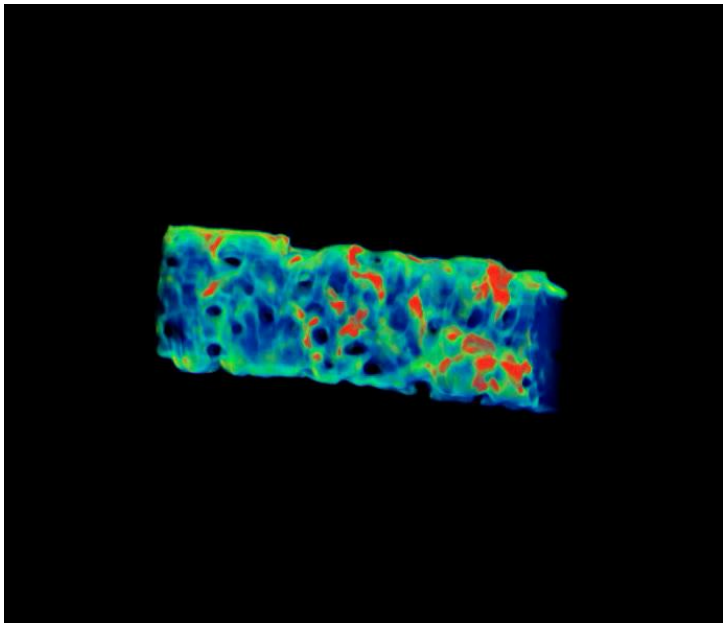
# In Situ TEM: combination with tomography

## 3D study of capsule shell




STEM imaging of outer porous surface

Lift out part of the shell with FIB

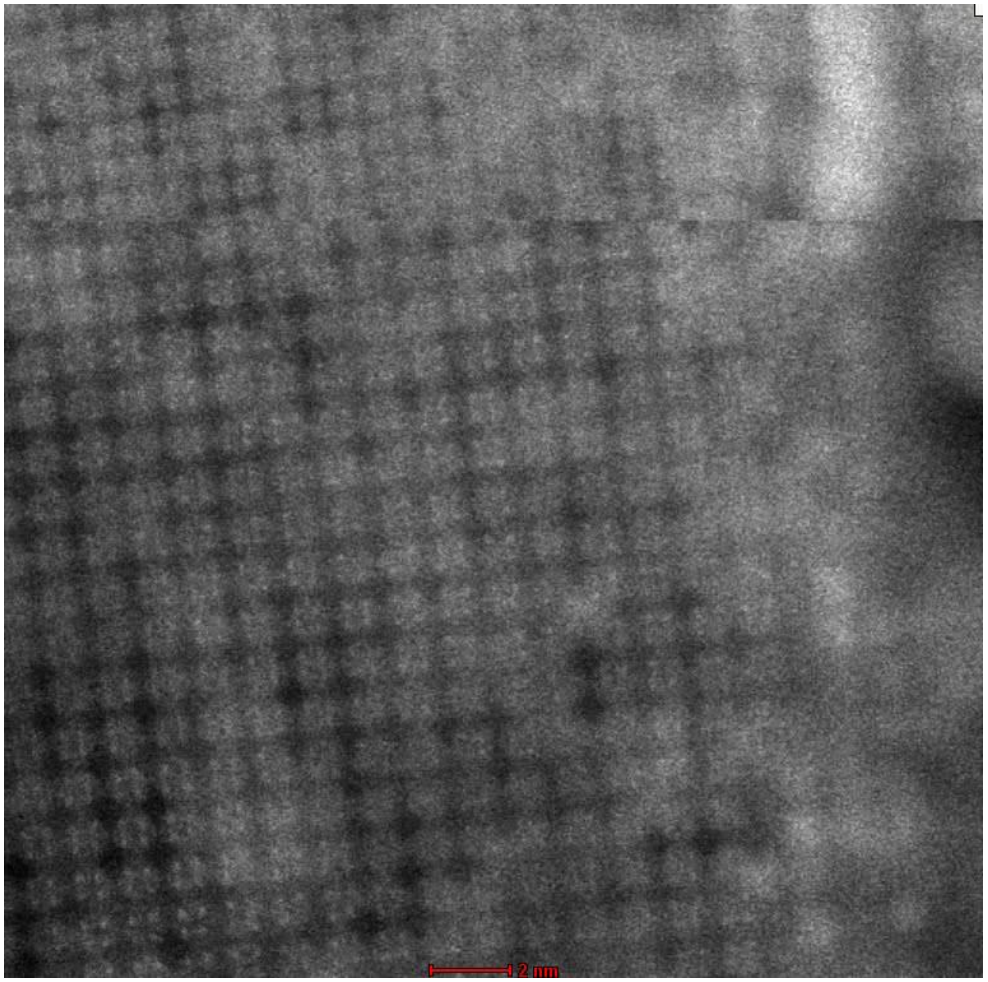


Visualizing channels throug electron tomography

*Heidari et al., Microscopy and Microanalysis, 22,:1222-1232 (2016)*

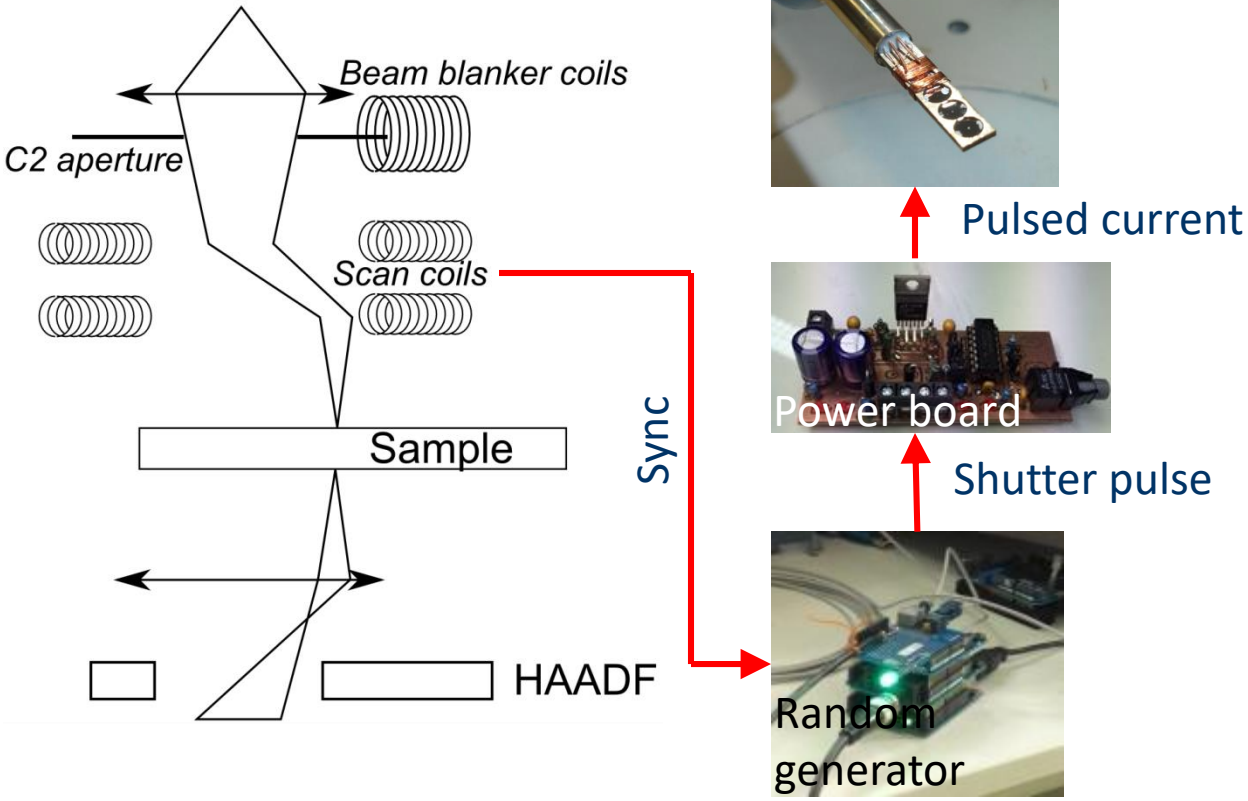
# Beam sensitive materials

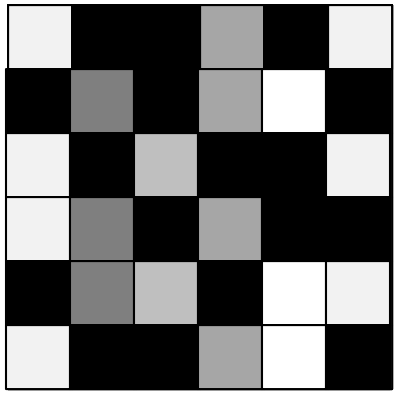
## Effect of beam on zeolite



# Beam sensitive materials

## Implementation of compressed acquisition in a TEM



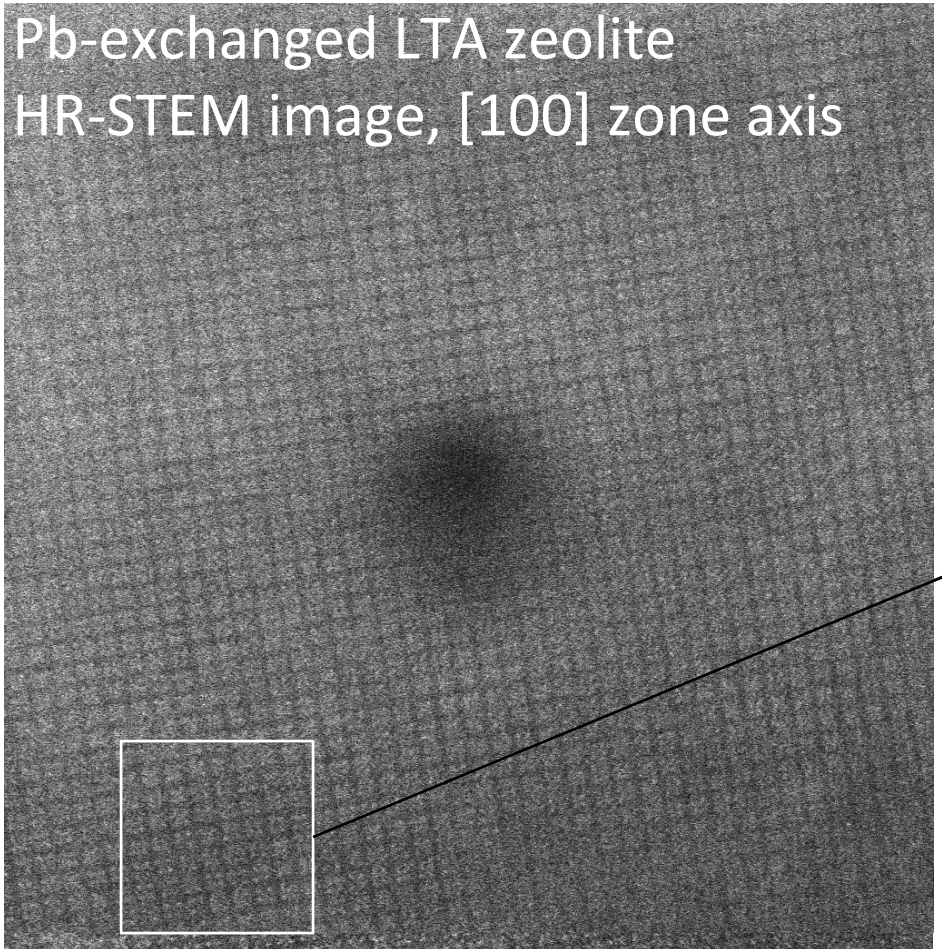



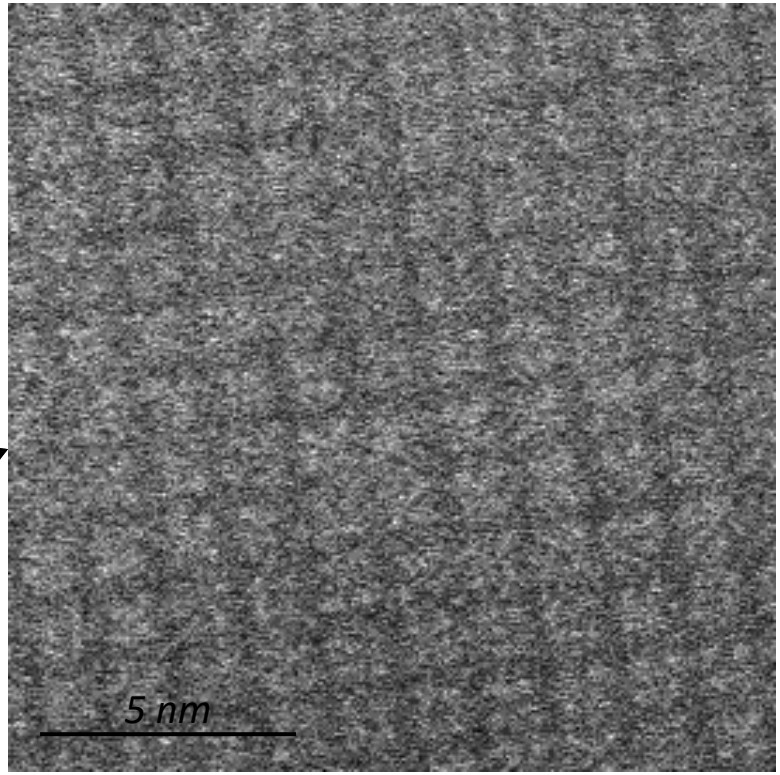
Acquired Image

*Buban et al., Journal of Electron Microscopy 59(2):103-112 (2010)*
*Stevens et al, Microscopy 63(1): 51-51 (2014)*

# Beam sensitive materials

## Implementation of compressed acquisition in a TEM

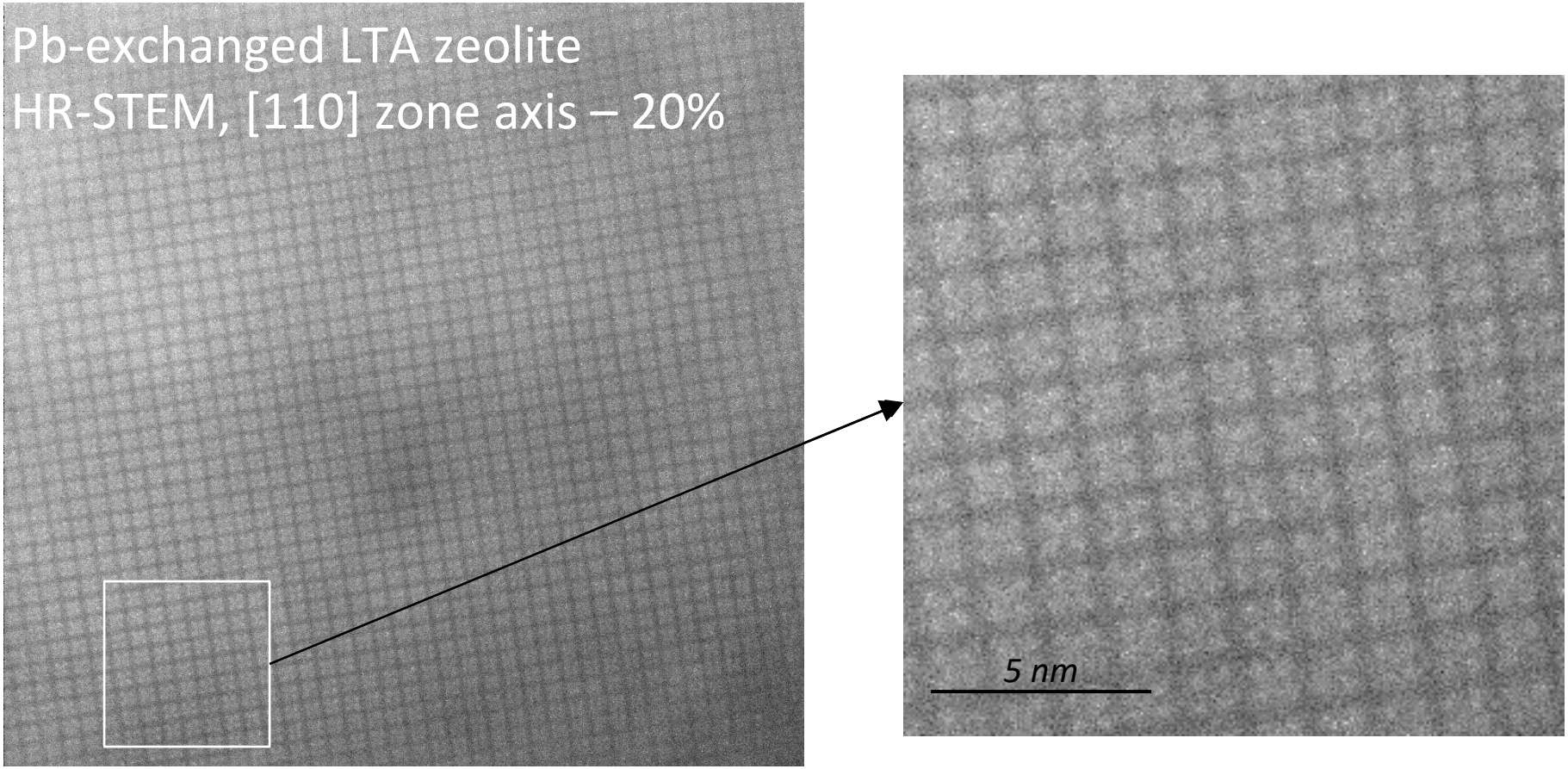



1.8Mx, dwell time 1 μs, 25 pA probe (664 $e^{-}.Å^{-2}$)

# Beam sensitive materials

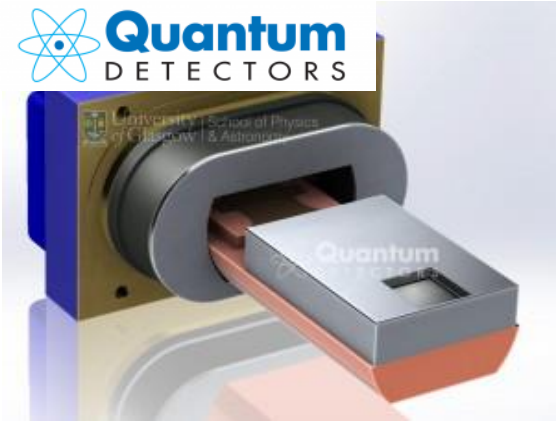
## Implementation of compressed acquisition in a TEM




1.8Mx, dwell time 10 µs, 25 pA probe (1328 $e^{-}.Å^{-2}$)

# Future developments

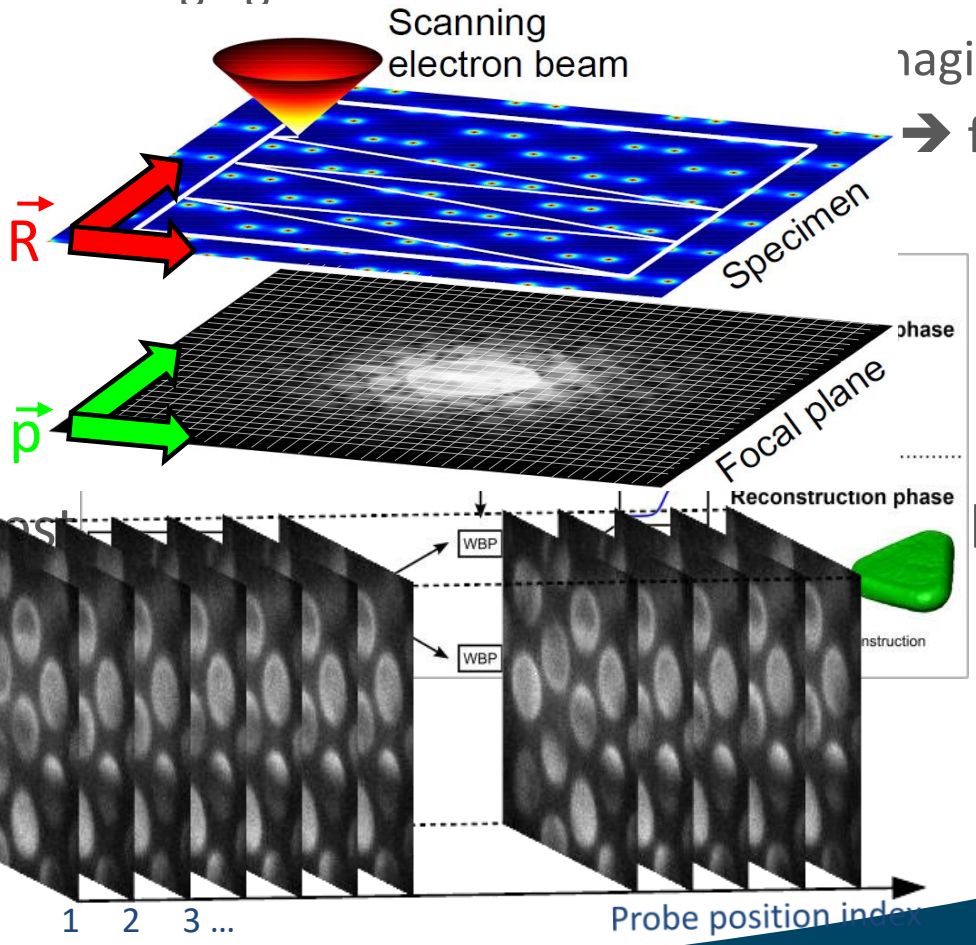
- Novel direct electron detectors (4D STEM)




**Medipix3 Merlin**

**Experimental setup**

- Imaging of beam sensitive materials ➔ ıaging)
- ➔ fast




- In situ TEM: strength test l
  biasing, gas flow and

**„4D data set“**

**Contact info:**
**alexander.neirinckx@uantwerpen.be**

University of Antwerp
NANOcenter
IOF consortium

Electron Microscopy
for Materials Science

CMT
Condensed Matter Theory

PLASMANT
Plasma, Laser Ablation and
Surface Modelling Antwerp

Universiteit
Antwerpen

# EMAT: equipment

## Electron Microscopes:

### 2 Titan-cubed

- TEM + STEM (HAADF, ABF)
- Spatial resolution: 0.05 nm in TEM and 0.08 nm in STEM
- Acceleration voltage between 60-300 kV
- EELS with energy resolution: < 0.2 eV
- Highly efficient EDX system (atomic resolution)
- 3D imaging in tomography
- Remote control

### Tecnai G2

- Electron diffraction (SAED, CBED)
- Orientation mapping (ASTAR)
- High resolution TEM and HAADF-STEM
- EDX

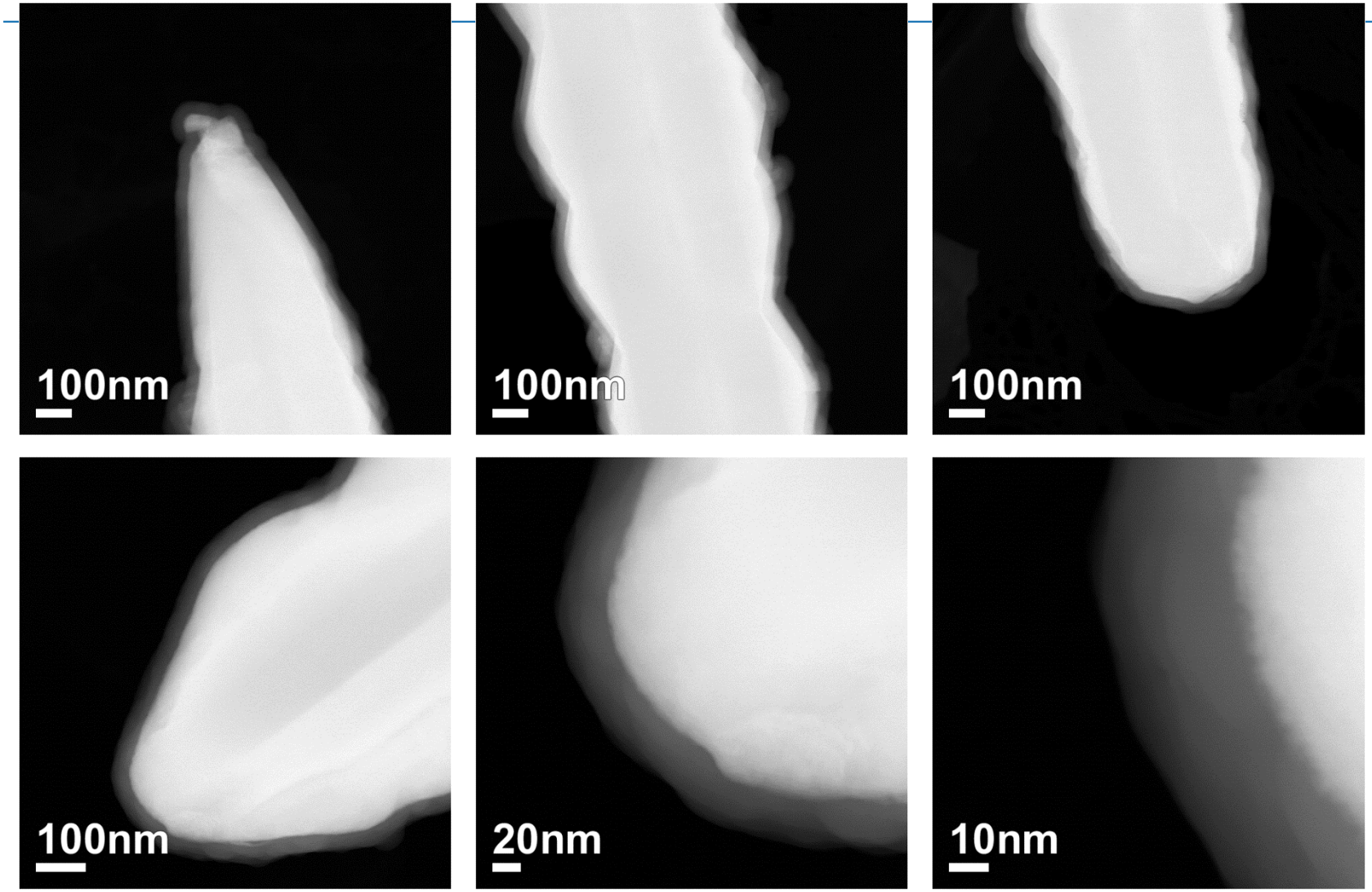
### Osiris

- High resolution TEM and HAADF-STEM
- Highly efficient EDX system
- EELS

### Focused ion beam & 2 Scanning Electron Microscopes

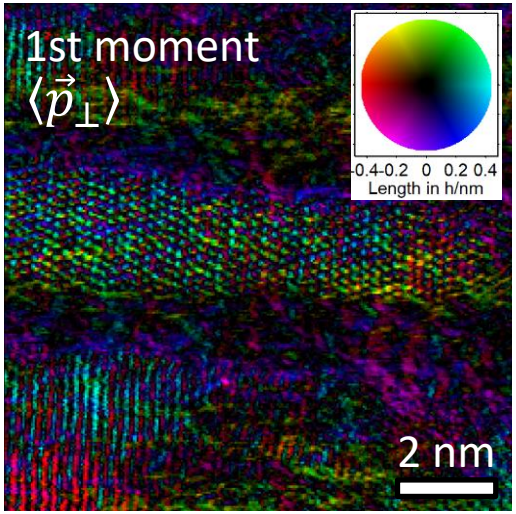
- Slice and view
- ESEM with EDX/WDX system
- TEM sample prep.

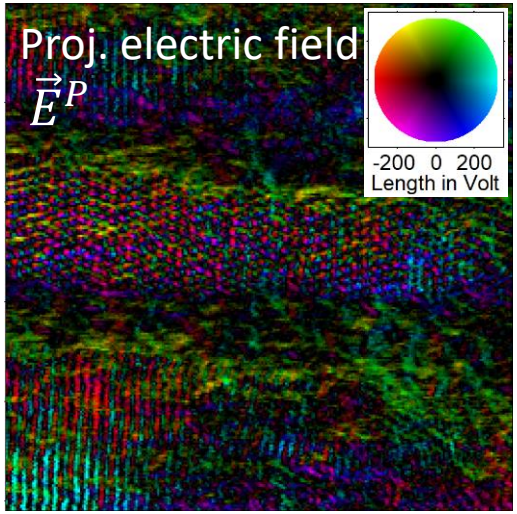
# HAADF-STEM images

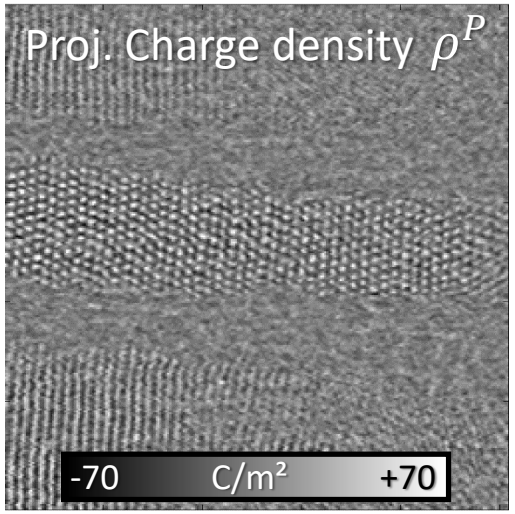


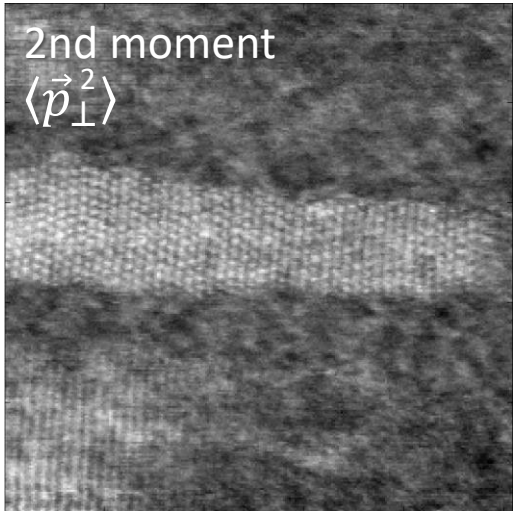

HAADF-STEM images show the presence of the coating.

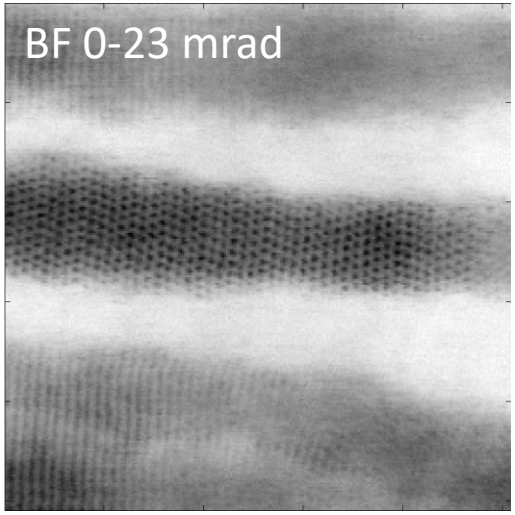
# Exploring momentum space: *Au Nanowires, Medipix*

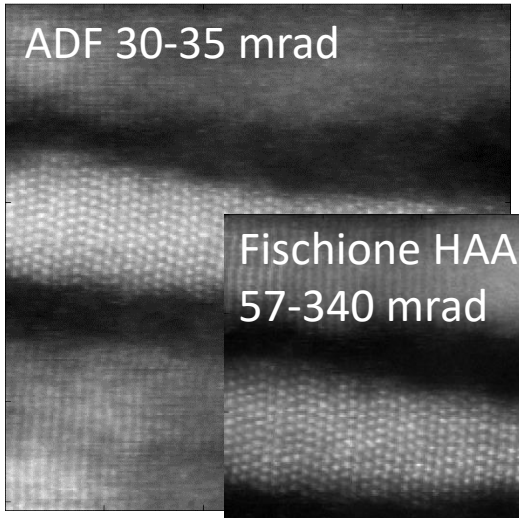


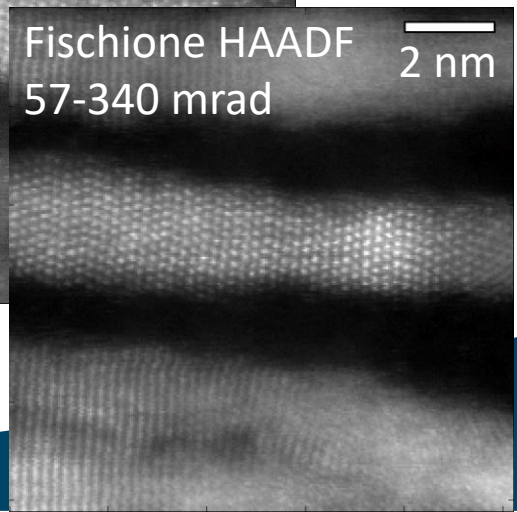



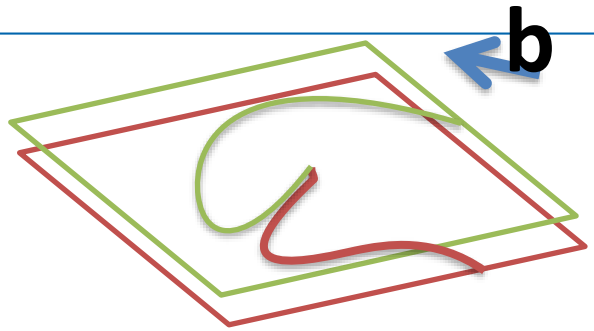



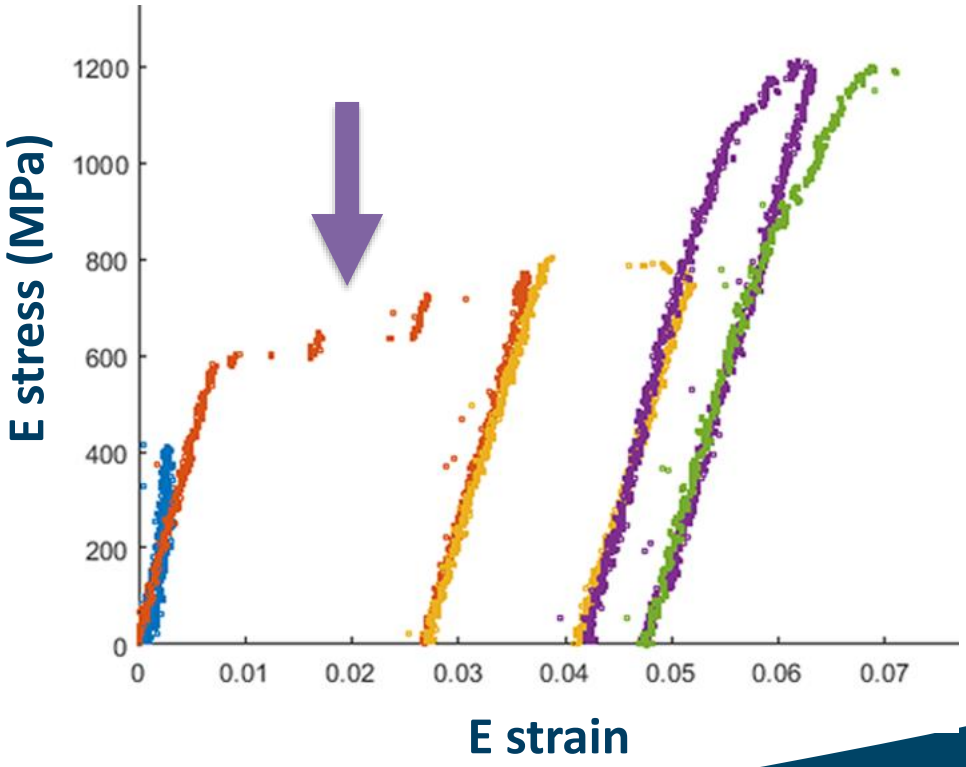



# In situ TEM: nano tensile test

## Push to pull experiments

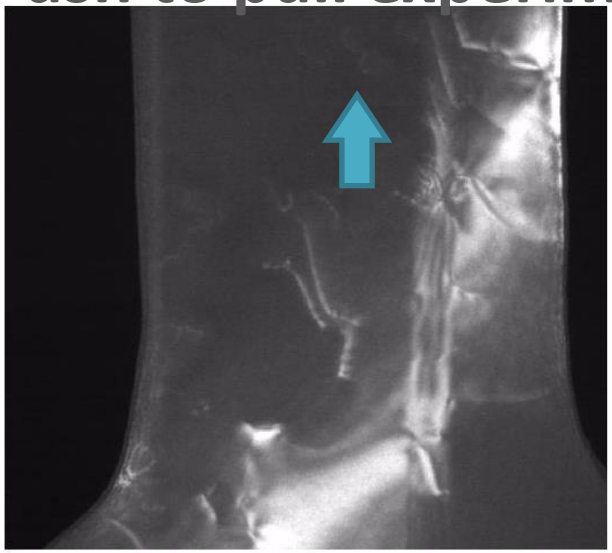


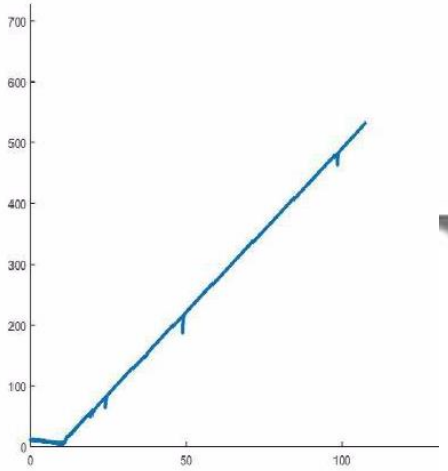

High activation of a spiral dislocation

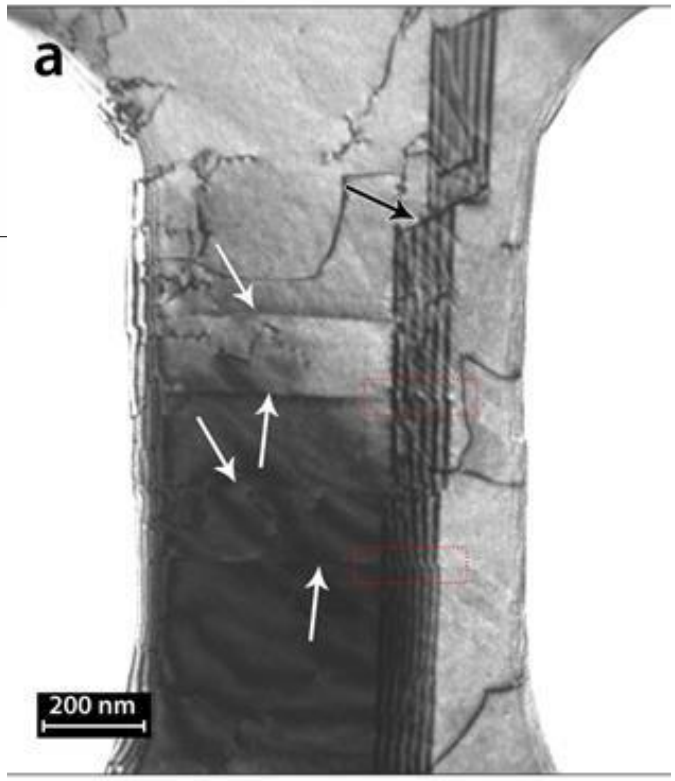


# In situ TEM: nano tensile test

## Push to pull experiments






Cross slip of dislocations in twin boundary

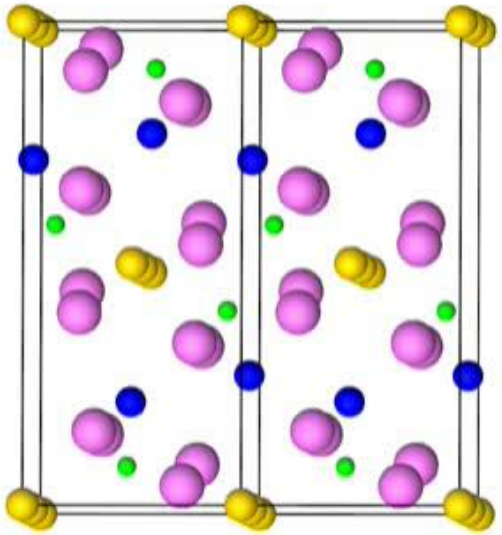
# Diffraction tomography

## Determining crystal structure

Specimen: ~100-200 nm single crystal

Data: electron diffraction patterns acquired during tilting of a crystal

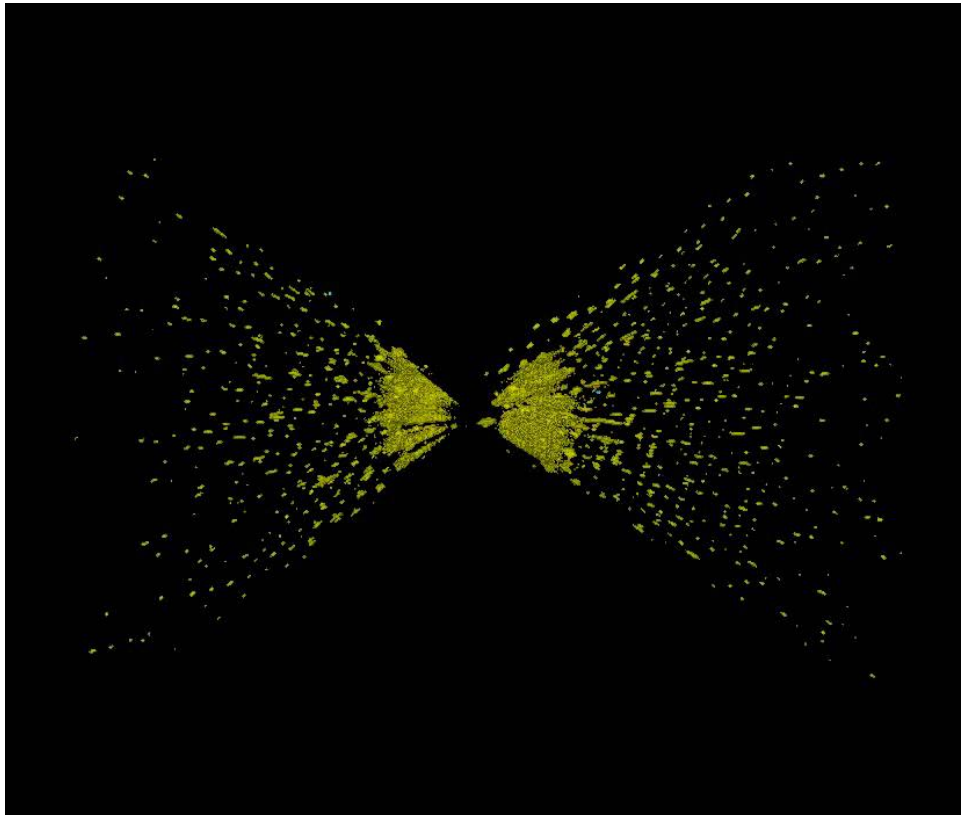
Diffraction tomography of $LiFePO_4$



# Diffraction tomography

## Determining crystal structure

Reconstruction of reciprocal space

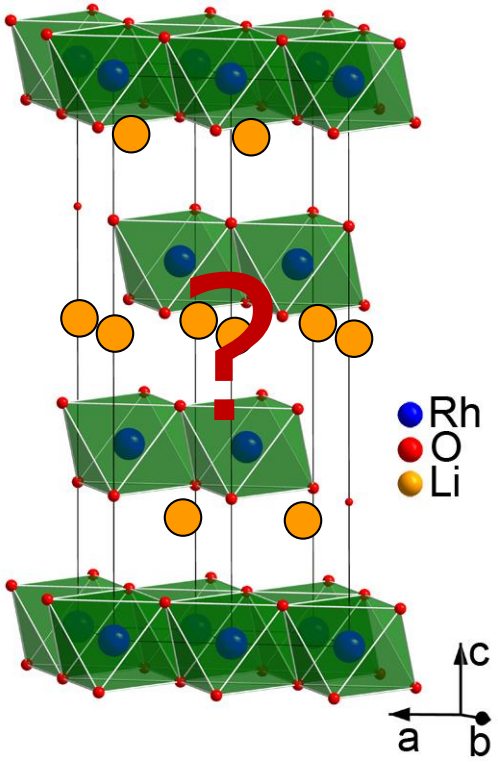


- Determine crystal structure without prior-knowledge
- Detect positions of light elements

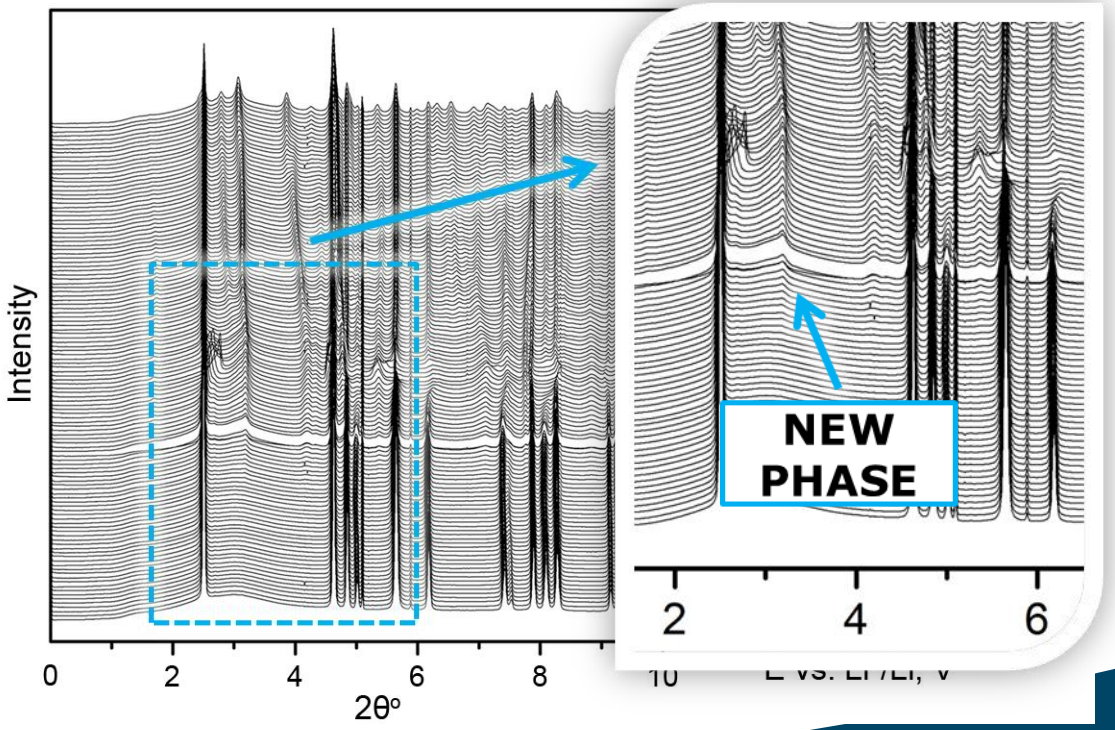
# Diffraction tomography

## Determining crystal structure

$LiRhO_2$ —charge (-0.45 $Li^+$)→ $Li_{0.55}RhO_2$ (3.85 V) —charge (-~0.45 $Li^+$)→ $Li_xRhO_2$ (4.1 V)

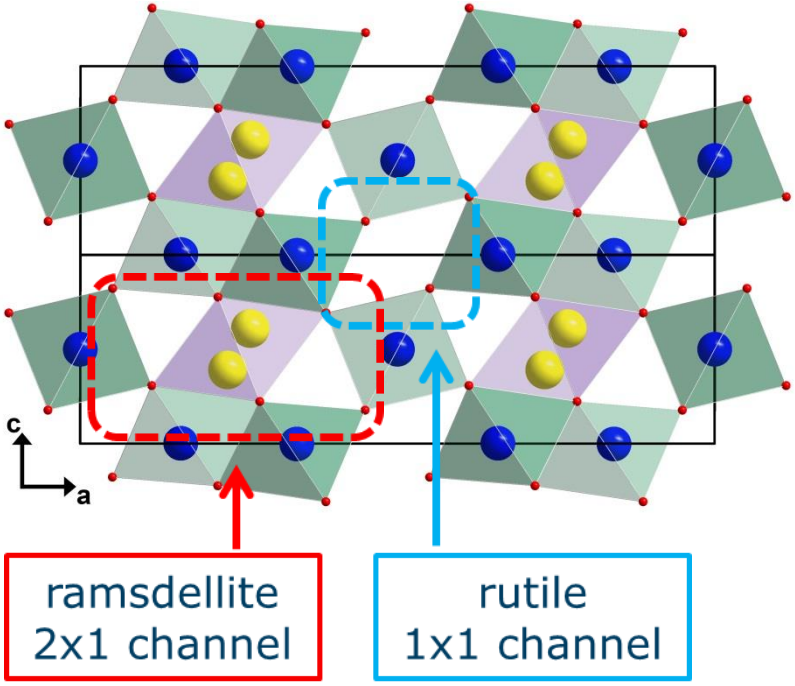



In-situ synchrotron powder diffraction in electrochemical test cells



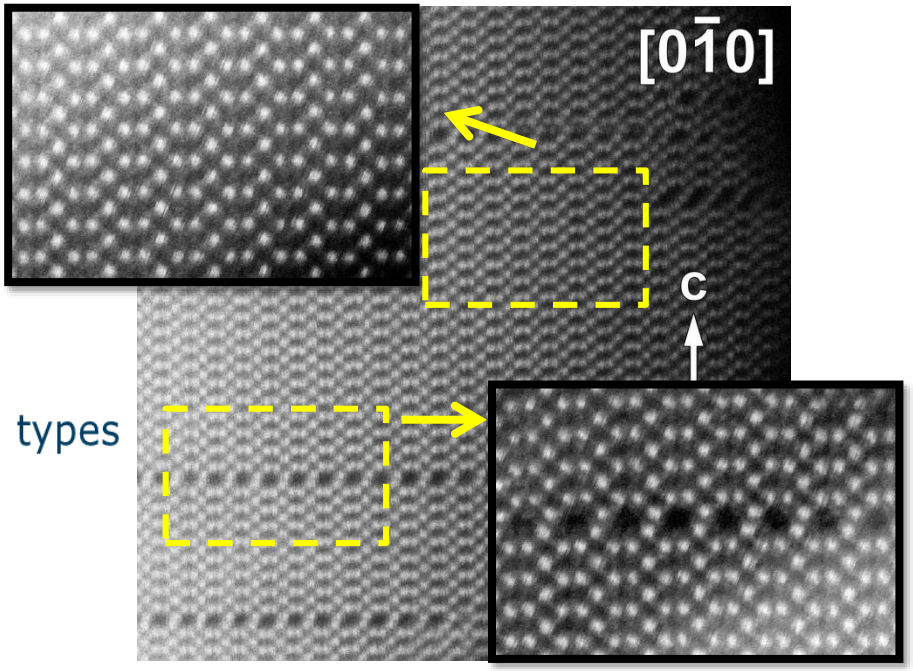
# Diffraction tomography

## Determining crystal structure




Applied techniques:

- SAED and electron diffraction tomography
- Monte Carlo method for optimization of Li positions




Structure solution: 3D structure with 2 channel types

C2/m
a=14.188(2) Å
b=3.0740(2) Å
c=4.5050(7) Å
β=92.087(8)°

Rf = 0.268