CISCEM 2016
3rd International Conference on In-Situ and Correlative Electron Microscopy
October 11-12, Saarbrücken/Germany

Rapid Tomography in Environmental TEM: How Fast Can We Go to Follow the 3D Evolution of Nanomaterials in situ?

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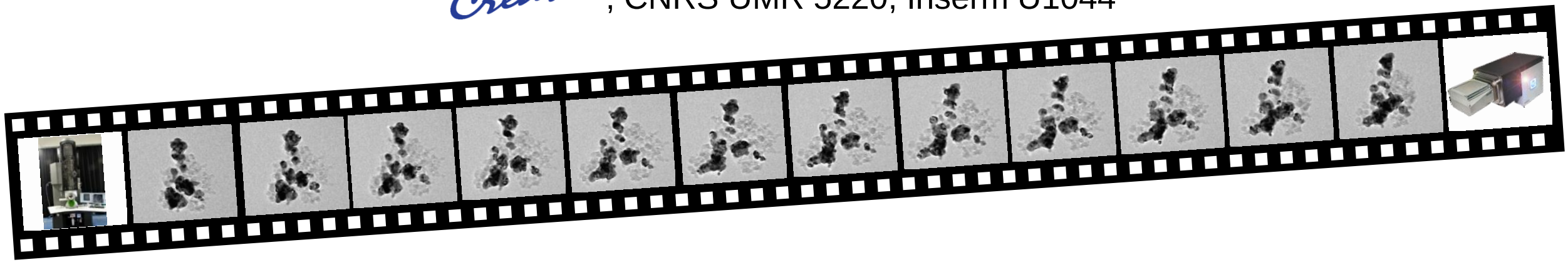
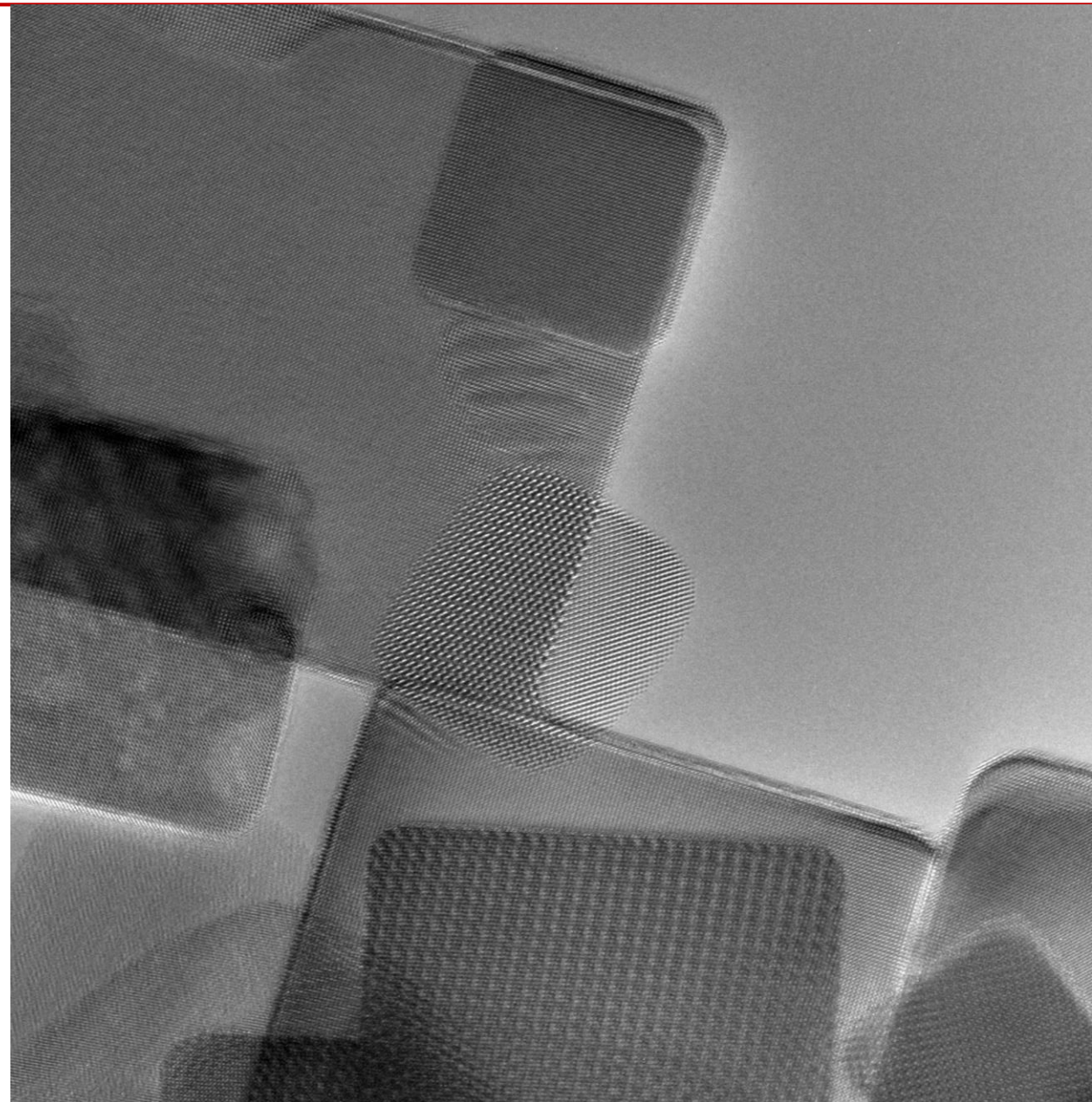


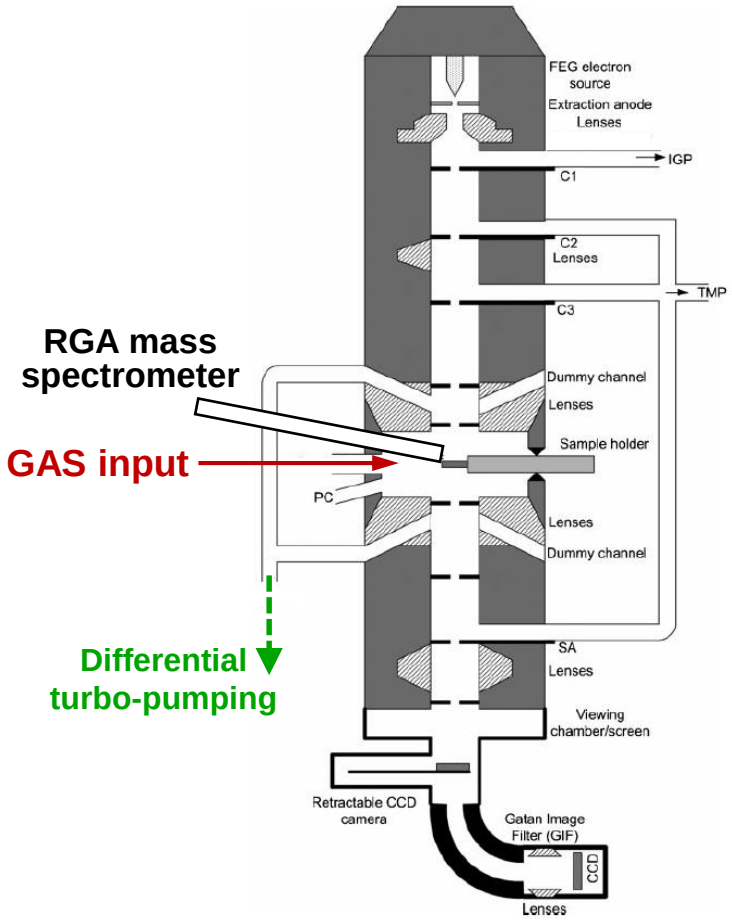
OUTLINE

- **Experimental Background on ETEM**
- **Fast 3D acquisitions**
  (Towards very fast tomography at the second level)
- **Perspectives** (and conclusions)**:**
  3D Operando ETEM



Experimental background on ETEM

● Environmental microscope (differential pumping system)

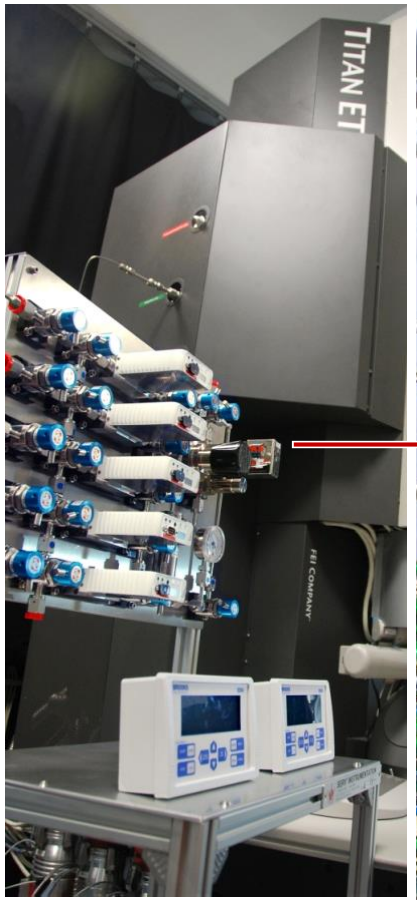


P. GAI et al., *MRS Bulletin* **33** (2008) 107

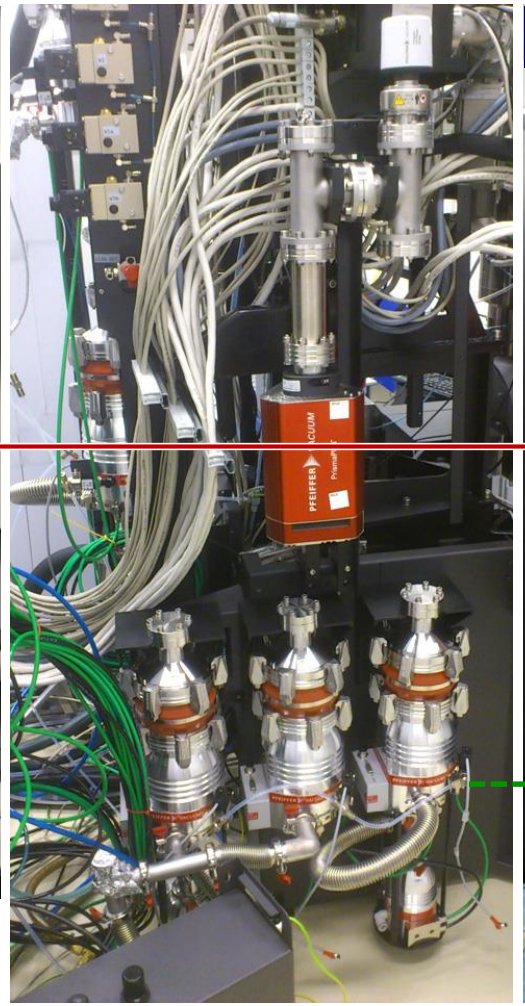
T.W. HANSEN et al., *Mat. Sci. & Technol.* **26** 11 (2010) 1338

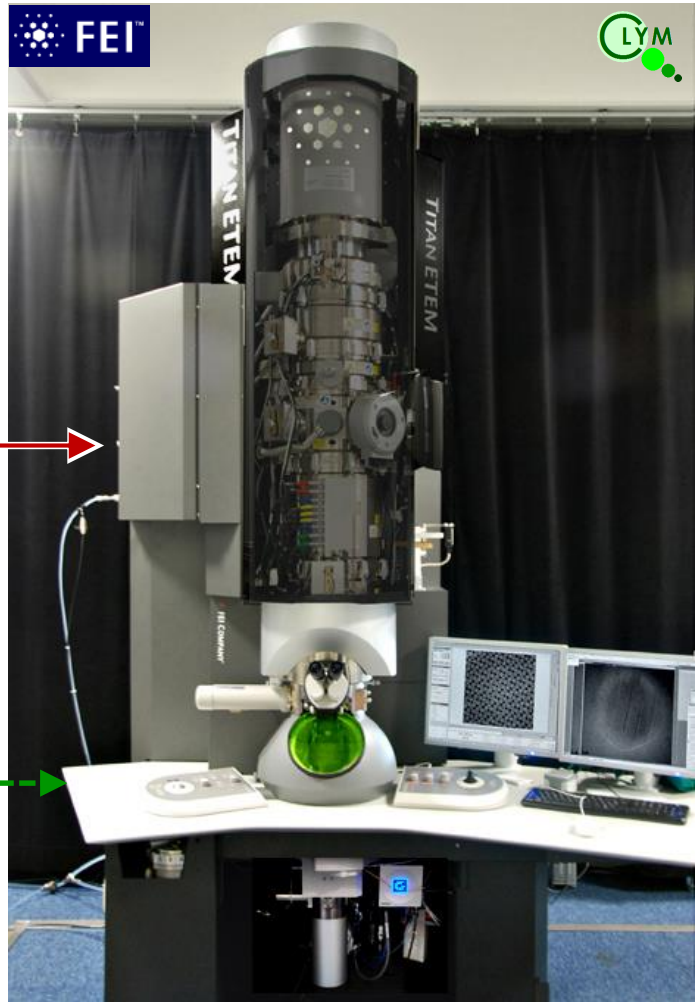
Dedicated Environmental TEM (≈ 10^{-6} mbar / a few mbar)

Aberration-corrected 80-300 kV FEI Titan ETEM



Serv'Instrumentation





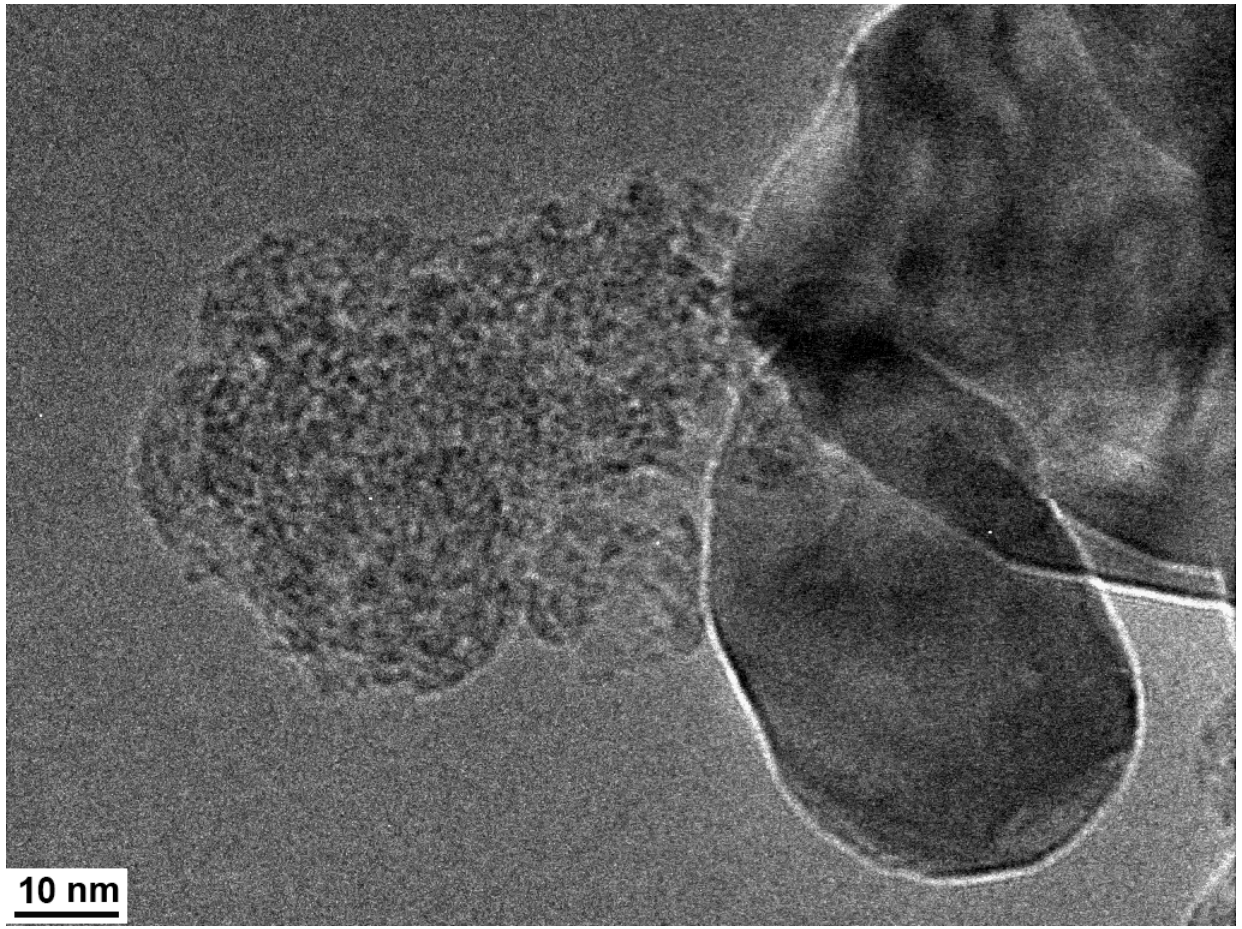
www.clym.fr

Experimental background on ETEM

- **Environmental microscope (differential pumping system)**

Dedicated Environmental TEM (≈ 10^{-5} mbar / a few mbar)
Aberration-corrected 80-300 kV FEI Titan ETEM

300 kV, T° = 495°C, 1.2 10^{-2} mbar O_2



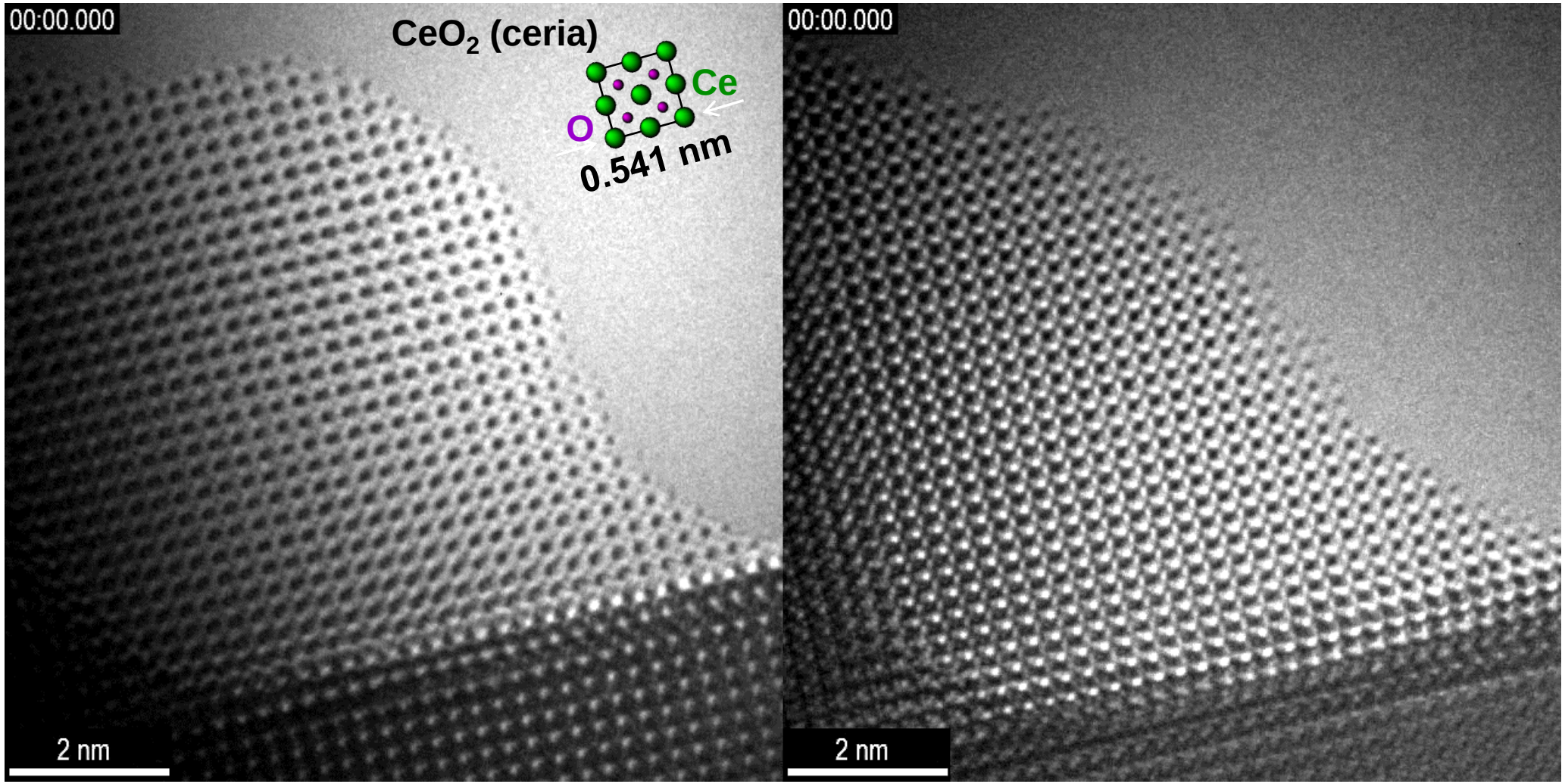
Speed x5, total time 4 min 13 sec

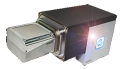
Combustion of soot on ZrO_2

A. SERVE et al., *Applied Catal. A* **504** (2015) 74-80

Surface effects: ‘gas-control’ of the atomic mobility

High Vacuum 1 10^{-6} mbar | **O_2 3 10^{-3} mbar**





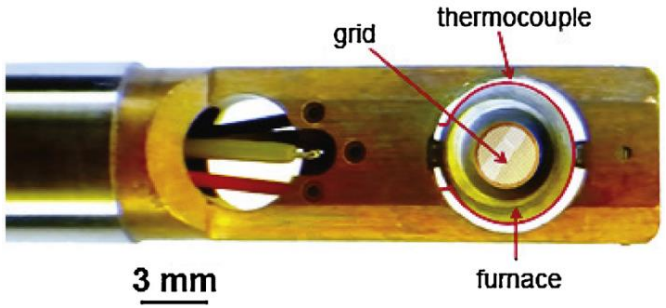
speed x0.2
103 fps
(2K images)

Thierry EPICIER, *Univ. Lyon*

Experimental background on ETEM

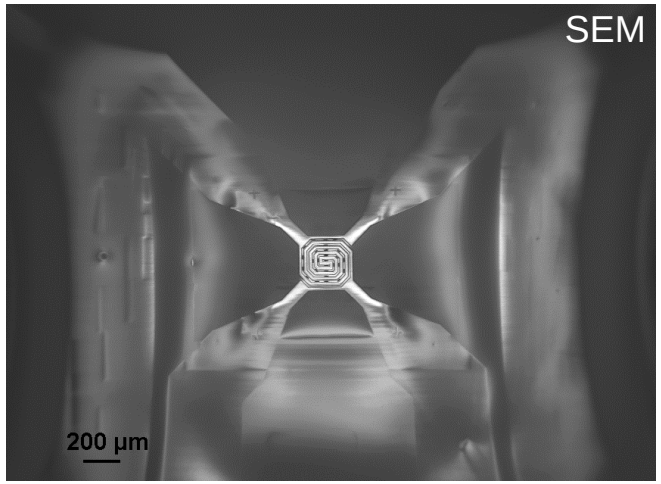
- **Heating sample holders**

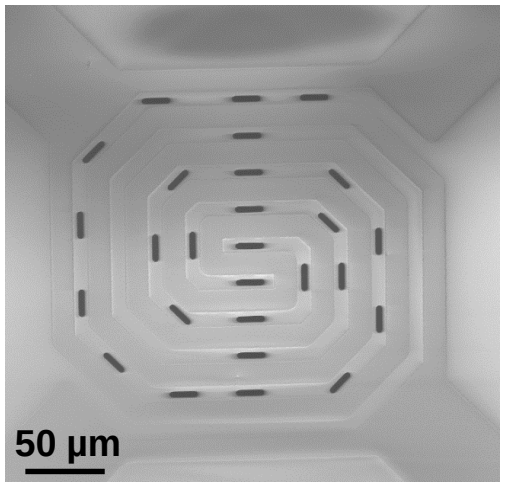
Furnace based GATAN™ ***(900°C)***
Shadowing over ±36°

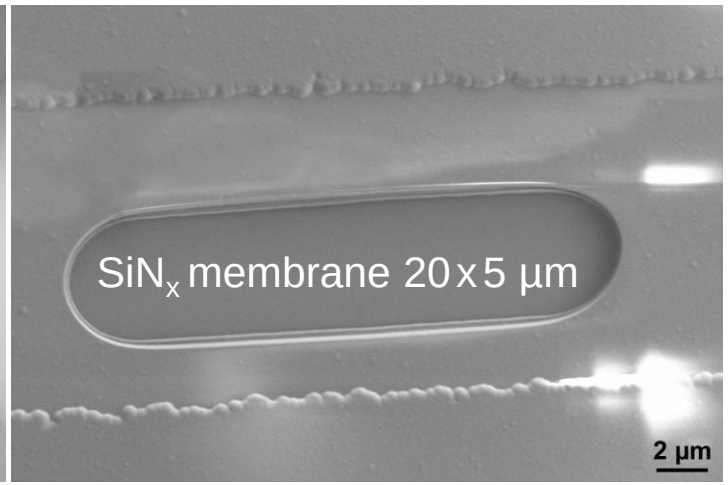


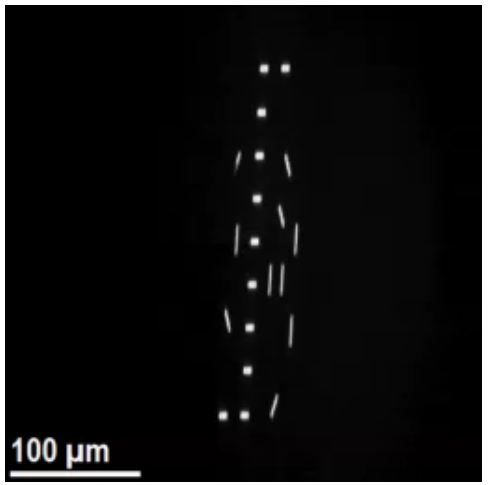
Wildfire S5 holder, DENS Solutions™
(MEMS-based SiN_x chips, 1300°C)

α tilt ± 72°



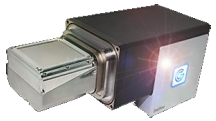






FAST 3D ACQUISITIONS
(Towards very fast tomography at the second level)

- ***Need for 3D analyses under environmental conditions***

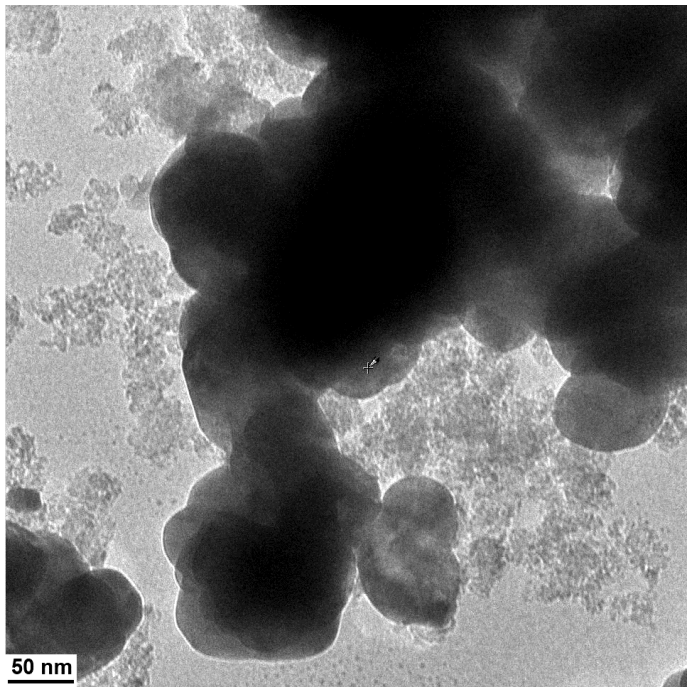


Oneview 4K camera

US1000XP-P 2K camera

GATAN

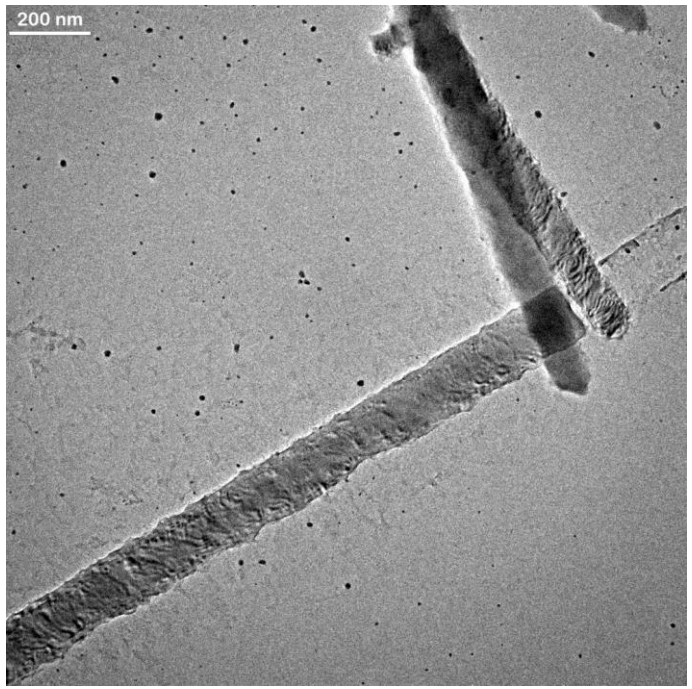
Combustion of soot on ZrO_2
ETEM 80 kV, 500°C, 3 mbar O_2



Total time **3 min 05 sec** (speed x10)

A. SERVE et al., *Applied Catal. A* **504** (2015) 74-80

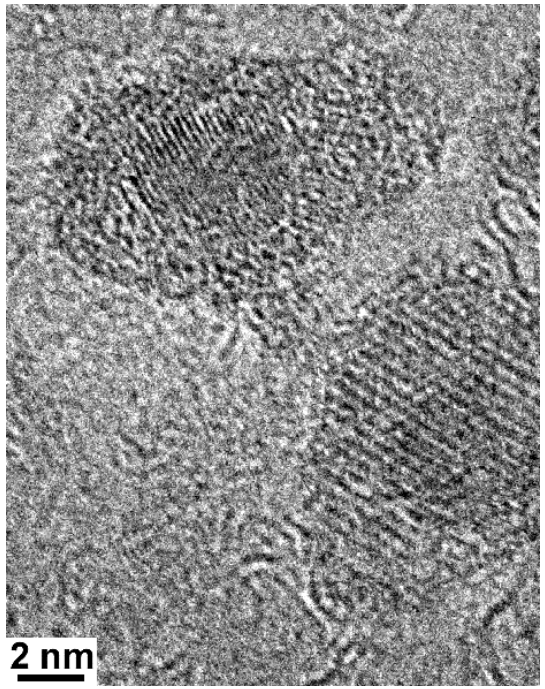
Melting of Si@Ge core-shell nanowires
ETEM 300 kV, 1100°C, HV



Total time **2 min 10 sec** (speed x10)

METSA experiment, 2016
(M.I. RICHARD, IM2NP)

Phase separation in $Ag@In_2O_3$ core-shell NPs
ETEM 300 kV, 450°C, 1.3 mbar H_2

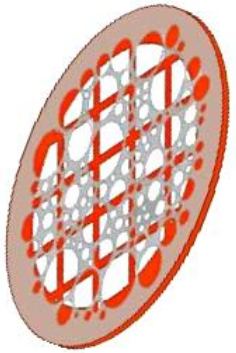


Total time **4 min 45 sec** (speed x20)

J. RAMADE et al., *to be published*

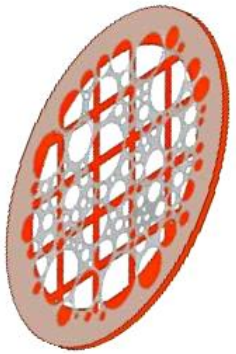
FAST 3D ACQUISITIONS
(Towards very fast tomography at the second level)

- ***Initial acquisition strategy: optimized 'step-by-step' tilt series***



Rotation angular amplitude: 2α	*140°*	*140°*
Elementary rotation step: $\delta\alpha$	*1°*	*2°*
Time for an elementary rotation: $t_{\delta\alpha}$	*1 sec*	*0.5 sec*
Pause after each rotation: t_{pause}	*0.5 sec*	*0.3 sec*
Acquisition time (exposure): t_{exp}	*0.2 sec*	*0.1 sec*
Total acquisition time: t_{total}	*≈ 4 min*	*≈ 1 min*

- ***Refined acquisition strategy: continuous rotation tilt***



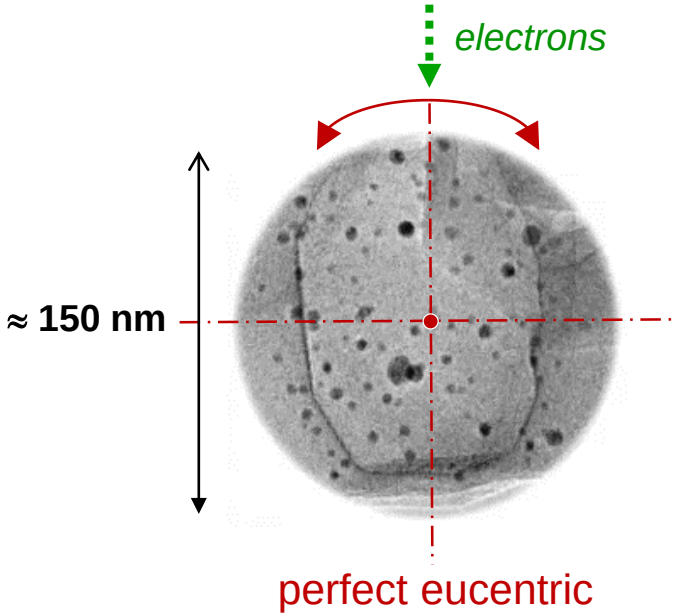
Rotation angular amplitude: 2α	*140°*	*140°*
Angular rotation speed ω	*1°/sec*	*4°/sec*
Total acquisition time: t_{total}	*2 min 20 sec*	*35 sec*

Thierry EPICIER, *Univ. Lyon*

FAST 3D ACQUISITIONS
(Towards very fast tomography at the second level)

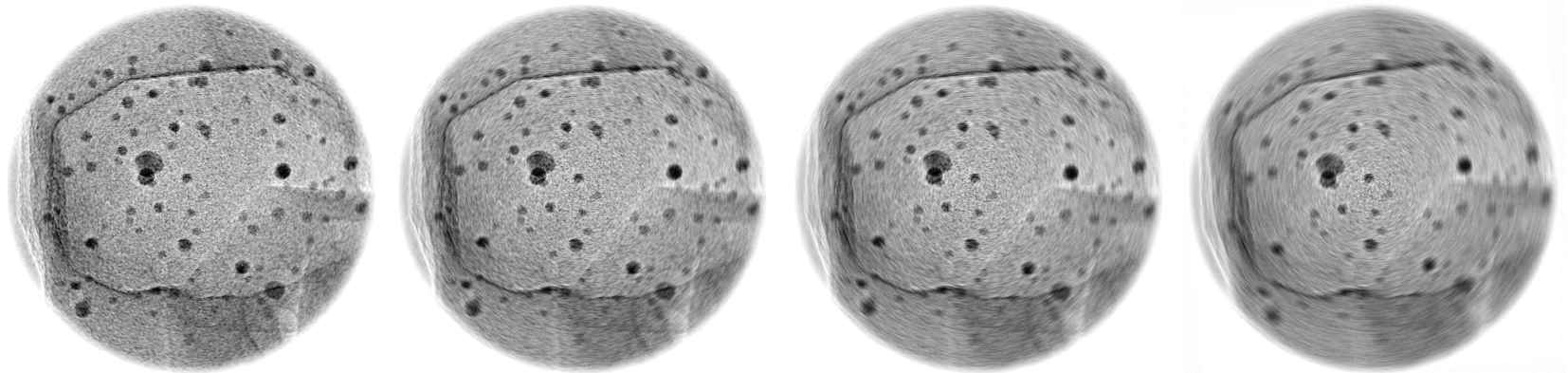
- **Evaluation of rotation-induced blur effects: *2D Ghost* for reconstruction**

*BF TEM image of **Ag NPs in mesoporous silicalites***



Rotation angular amplitude: 2α	140°	140°	140°	140°
Total acquisition time: t_{total}	30 sec	7 sec	5 sec	3 sec
Angular rotation speed $\omega = 2\alpha/t$	4.7°/sec	20°/sec	28°/sec	46.7°/sec
Number of frames per second: ***Fps***	5	10	10	10
Angular blur / frame: **Blfr** = $\frac{2\alpha}{t.Fps}$	0.93°	2°	2.8°	4.7°

Image at zero tilt



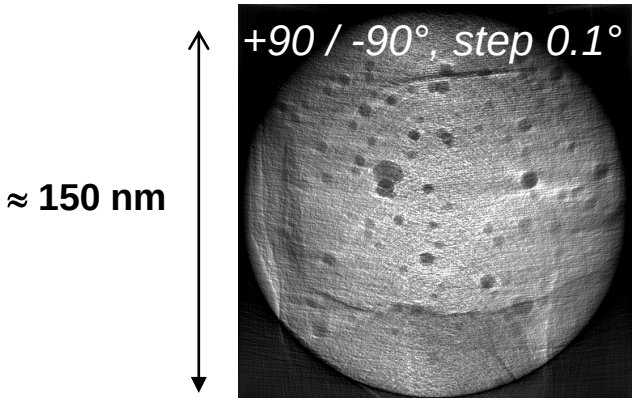
Blfr 1° **Blfr 2°** **Blfr 3°** **Blfr 5°**

FAST 3D ACQUISITIONS
(Towards very fast tomography at the second level)

- **Evaluation of rotation-induced blur effects: *2D Ghost* for reconstruction**

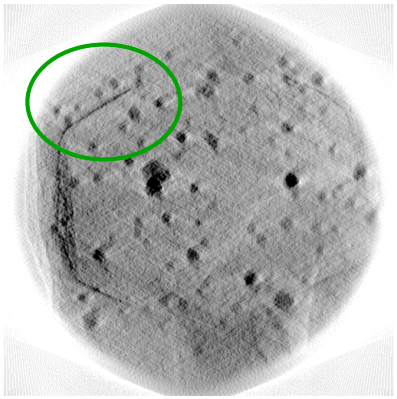
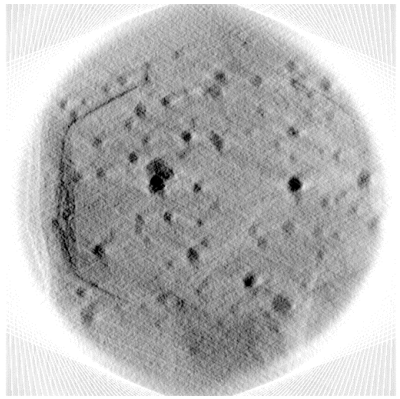
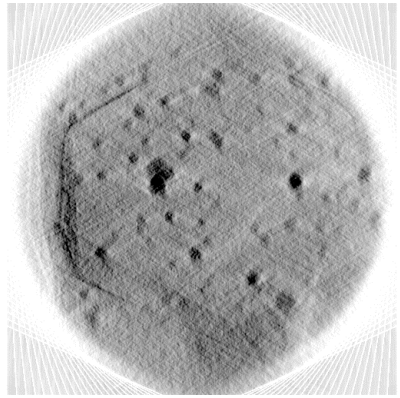
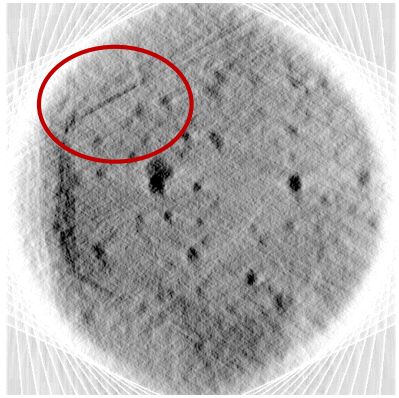
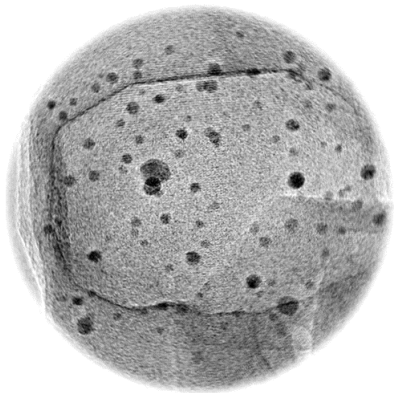
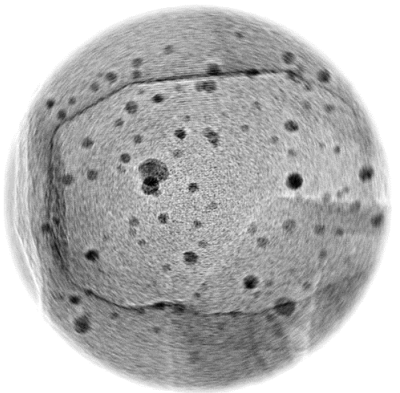
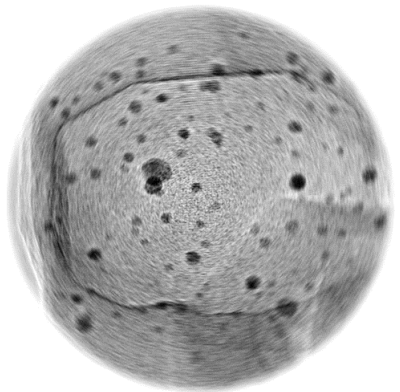
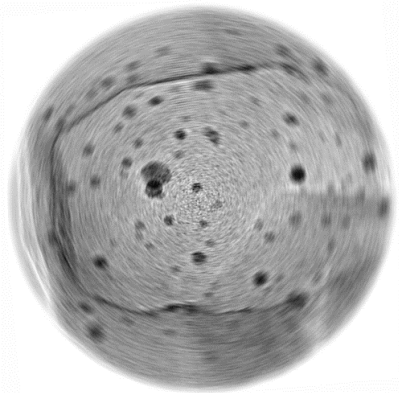
*BF TEM image of **Ag NPs in mesoporous silicalites***

‘PERFECT RECONSTRUCTION’



Weighted Back Projection

Image at zero tilt

+70 / -70°, **Blfr 1°**	*+70 / -70°*, **Blfr 2°**	*+70 / -70°*, **Blfr 3°**	*+70 / -70°*, **Blfr 5°**
			
			
Blfr 1°	**Blfr 2°**	**Blfr 3°**	**Blfr 5°**

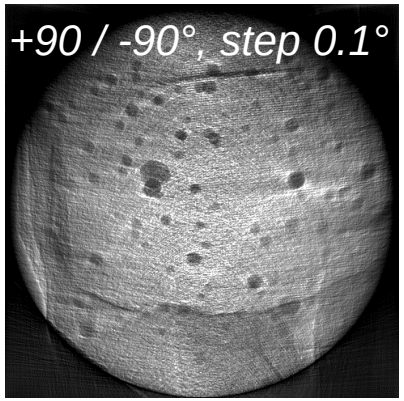
FAST 3D ACQUISITIONS
(Towards very fast tomography at the second level)

- **Evaluation of rotation-induced blur effects: *2D Ghost* for reconstruction**

*BF TEM image of **Ag NPs in mesoporous silicalites***

‘PERFECT RECONSTRUCTION’

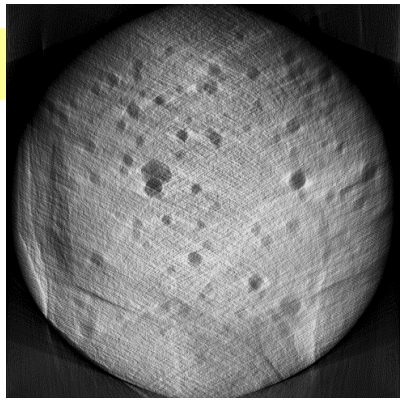
≈ 150 nm



Weighted Back Projection

Rotation angular amplitude: 2α	140°
Total acquisition time: t_{total}	5 sec
Angular rotation speed $\omega = 2\alpha/t$	28°/sec
Number of frames per second: *Fps*	100
Angular blur / frame: $\mathbf{Blfr} = \frac{2\alpha}{t.Fps}$	0.28°

+70 / -70°, **Blfr 0.3°**



Oneview GATAN
2K, 100 images/sec

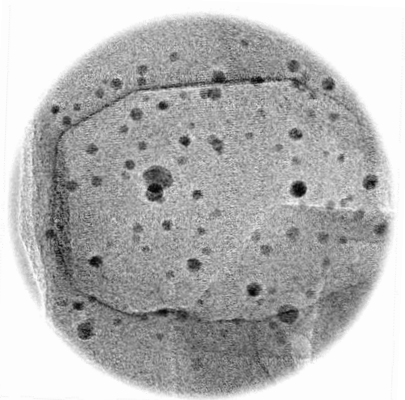
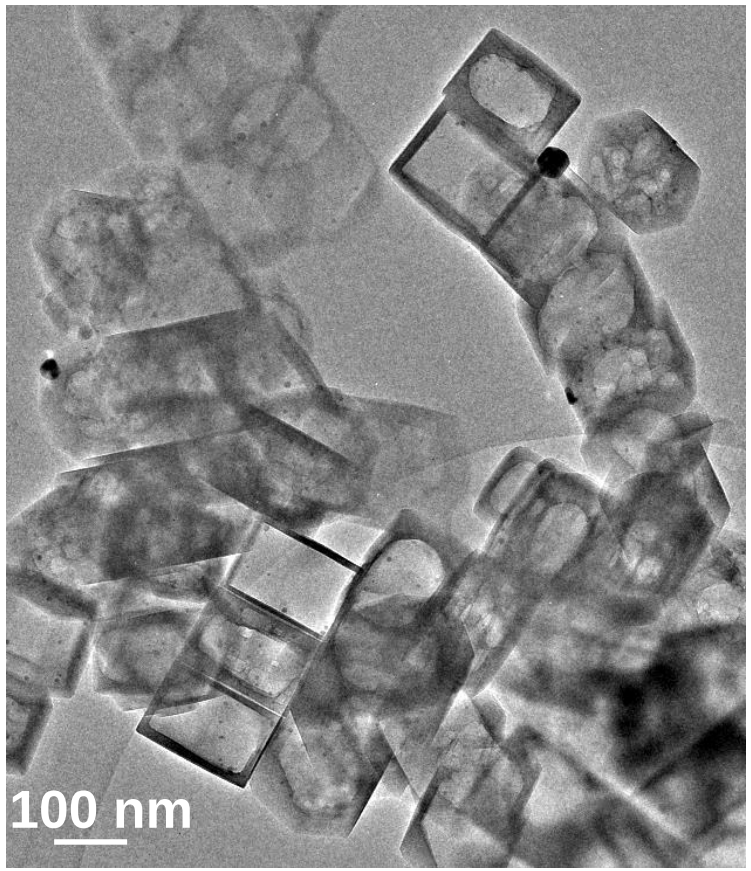


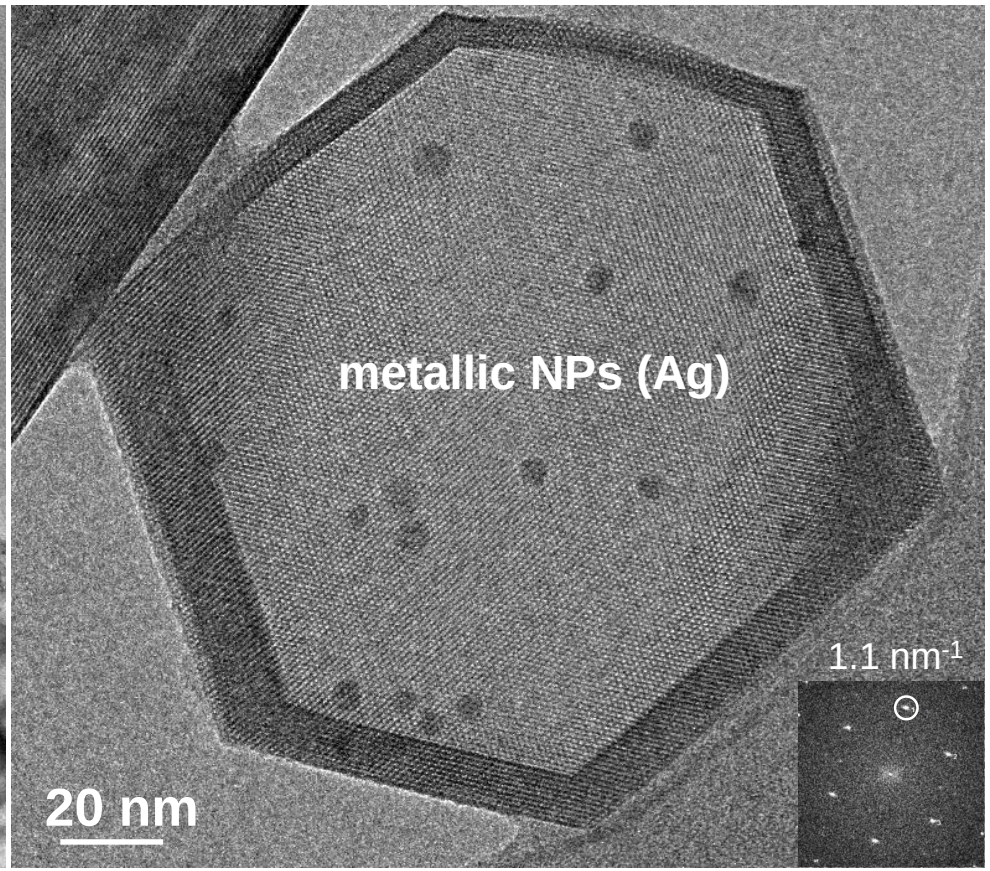
Image at zero tilt, Blfr 0.3°

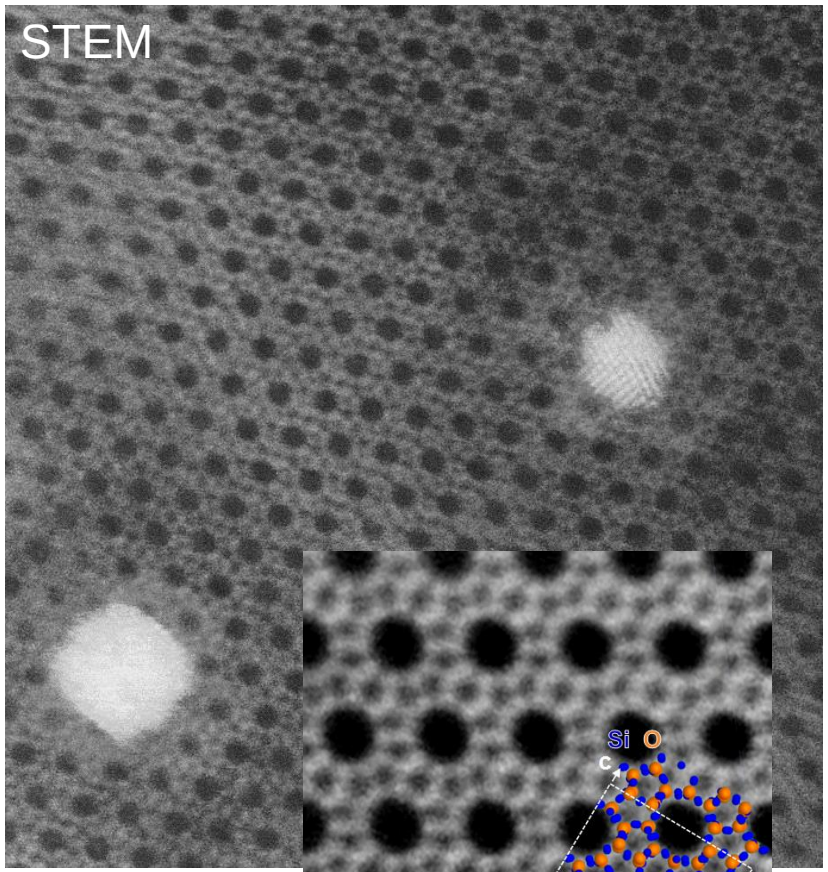
FAST 3D ACQUISITIONS
(Towards very fast tomography at the second level)

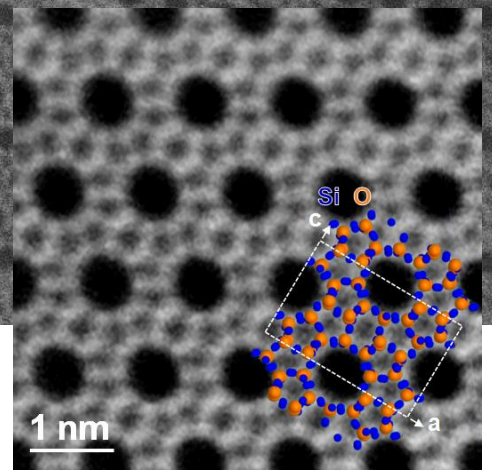
- **In situ calcination of *silicalites*-encapsulated metallic NPs (Ag)**
  Catalytic selectivity of molecules size through 'filtering' through the siliceous zeolite pores *(pore cut-off ≈ 0.7 nm)*

S. LI et al., *Chem. Commun.* **50** (2014) 1824-1826







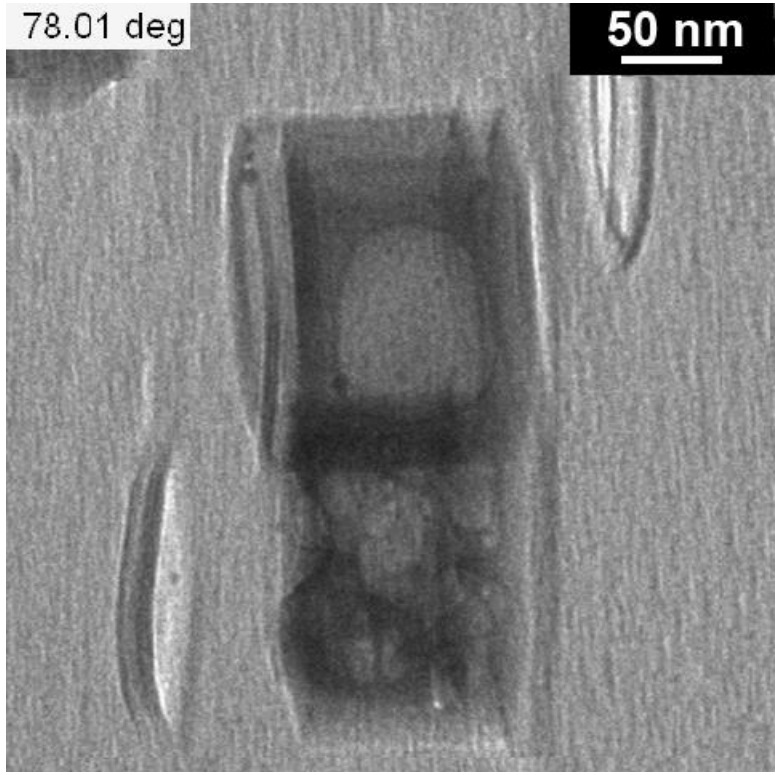


MFI orthorhombic structure
www.iza-structure.org

FAST 3D ACQUISITIONS
(Towards very fast tomography at the second level)

- **In situ calcination of *silicalites*-encapsulated metallic NPs (Ag)**

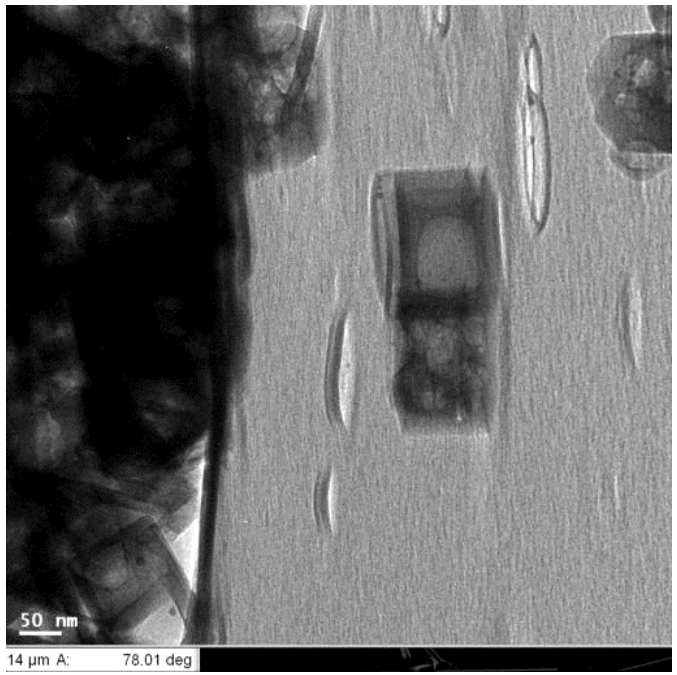
High Vacuum 20°C



speed x20

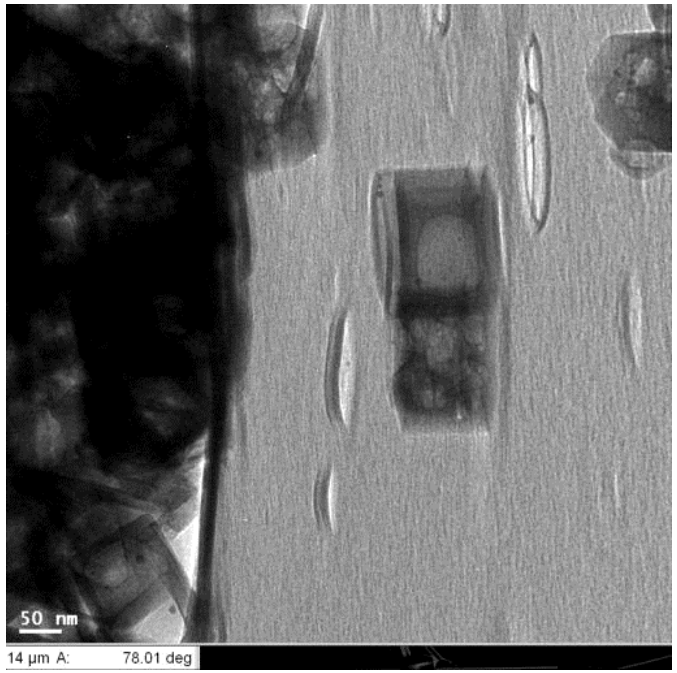
Aligned **tilt series 78° to -38° in 3 min 40 sec**
328 frames from a 1584 frames video sequence

screen video capture



speed x50

Raw **series 78° to -38° in 3 min 40 sec**
1584 frames



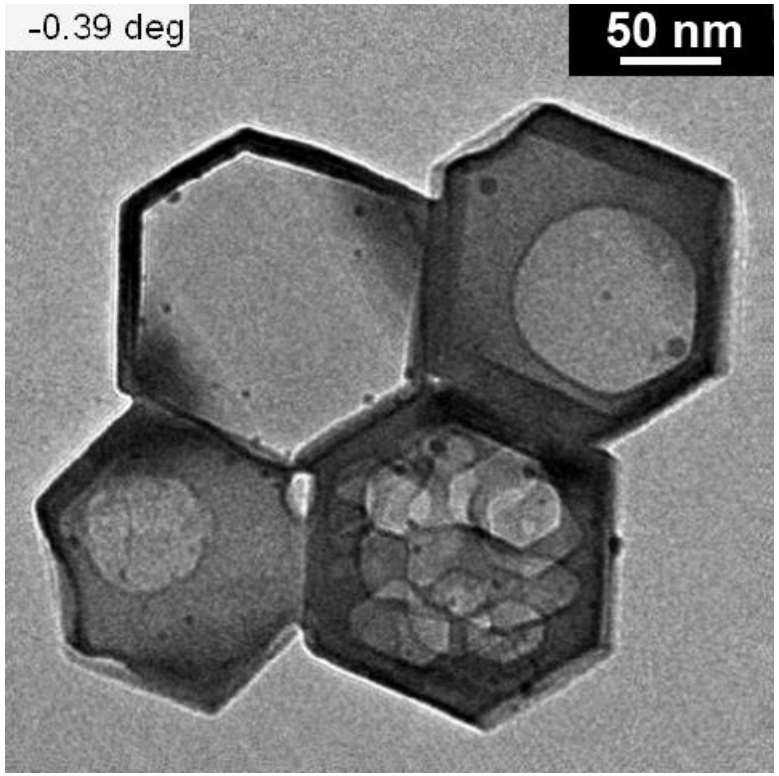
Post-mortem automatic detection and suppression of 'blurred' **images**
from 528 frames

Thierry EPICIER, *Univ. Lyon*

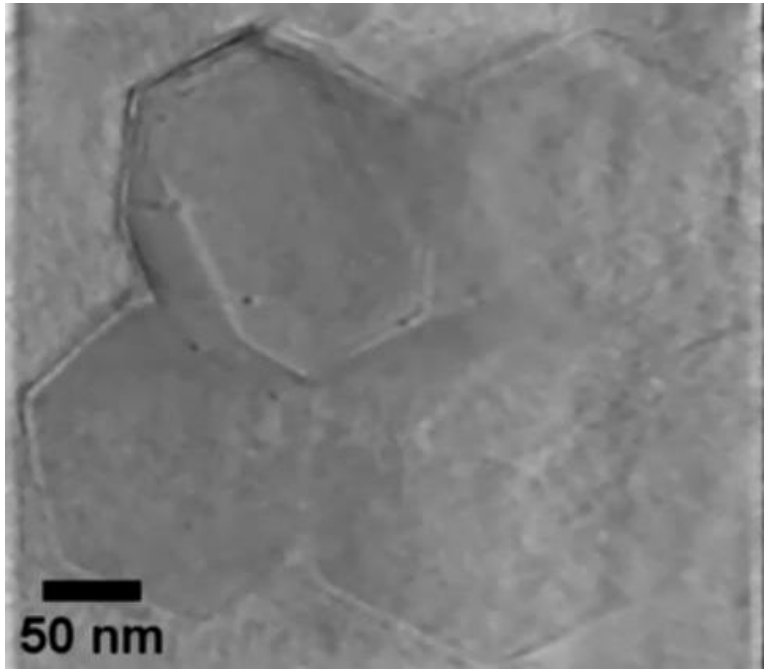
FAST 3D ACQUISITIONS
(Towards very fast tomography at the second level)

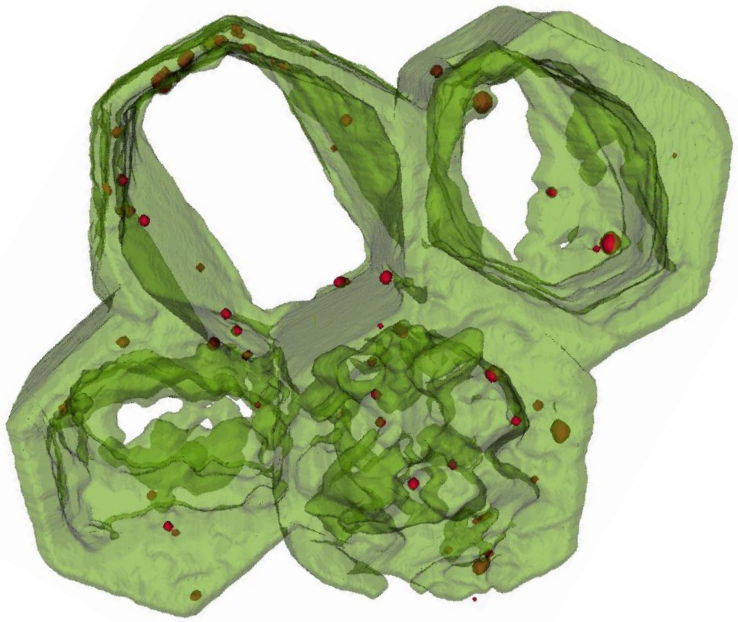
- **In situ calcination of *silicalites*-encapsulated metallic NPs (Ag)**

High Vacuum 20°C



Tomogram





3D model

- **In situ ETEM calcination (and 3D quantification) under O_2 up to 450°C:**
  results presented at IMC2014 T. EPICIER et al., *Proceed. IMC2014*, ISBN 978-80-260-6721-4

Some (ETEM) applications of fast tomography

- **Fast tomography of electron beam sensitive materials**

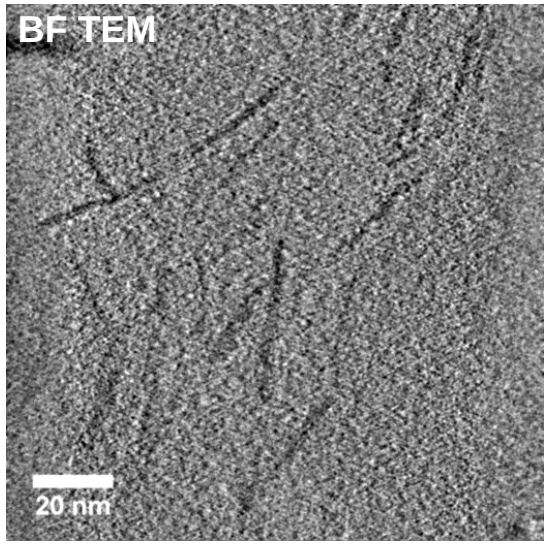
Ex. 1: **POLYMER NANOCOMPOSITES**
Dispersion of Mg_3AlCO_3 Layer-Double Hydroxide nanoplatelets in latex

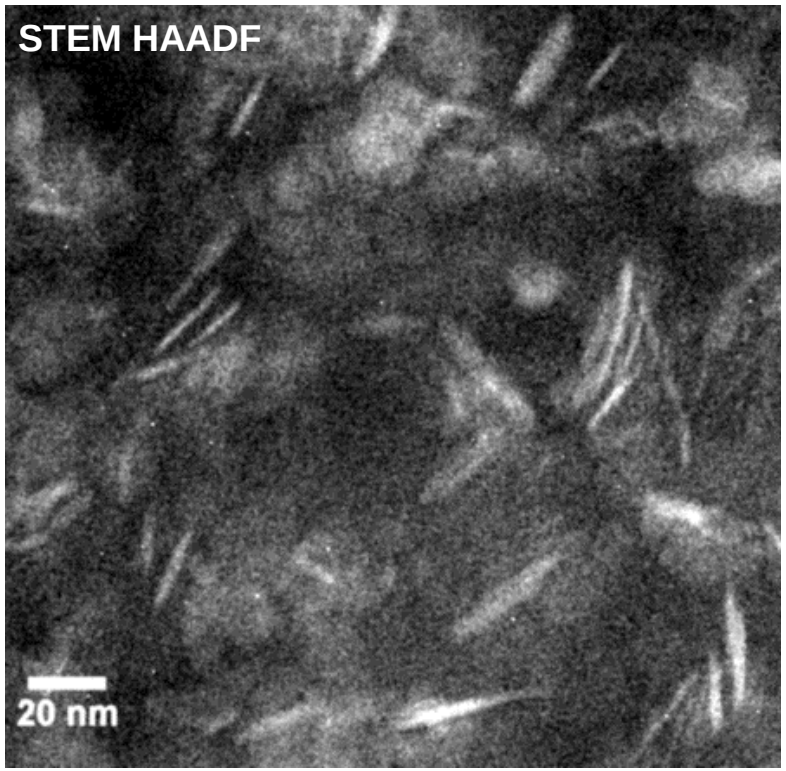
Latex balls stacking

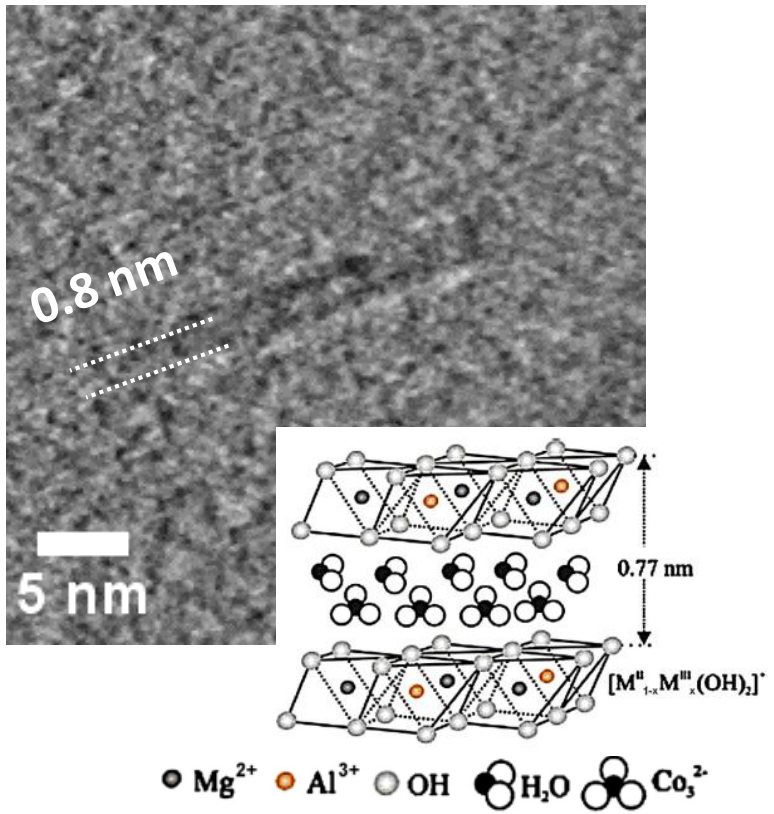
film formation →

Starch-Based Polymeric Materials and Nanocomposites, ed. J. AHMED, B. K. TIWARI, S. H. IMAM, M.A. RAO, *CRC Press*, (2012) 416 p.

TEM preparation by
cryo-ultramicrotomy (-62°C)
HV 20°C



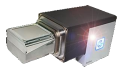




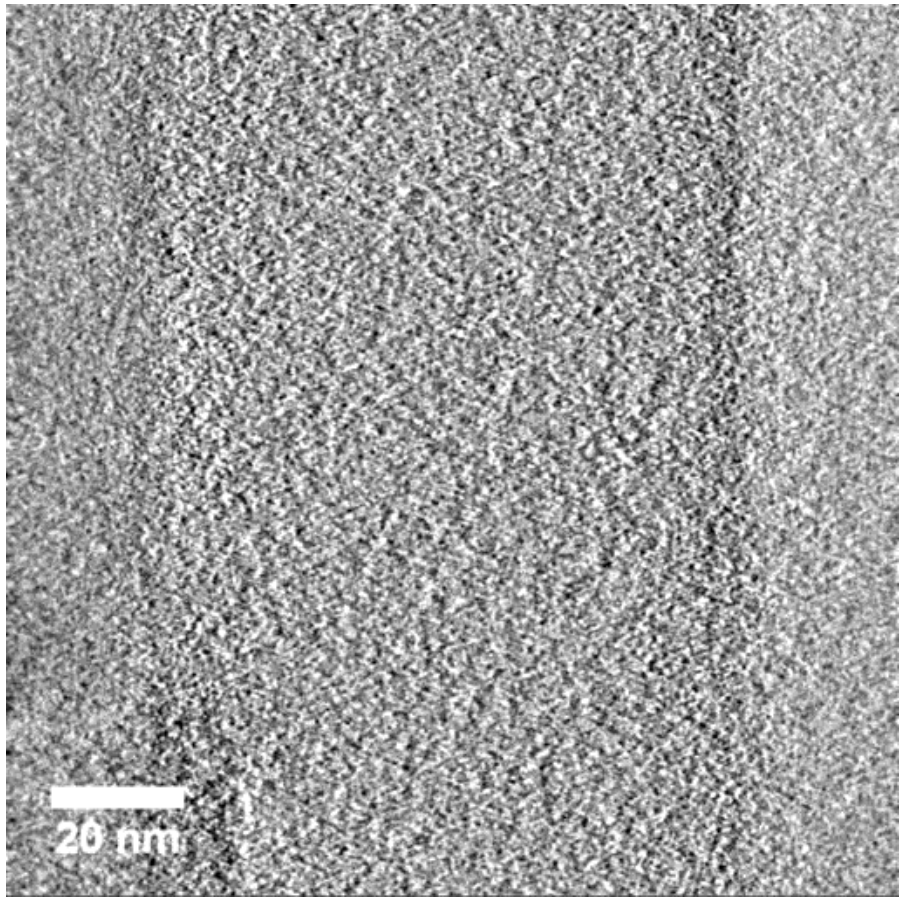
Some (ETEM) applications of fast tomography

- **Fast tomography of electron beam sensitive materials**

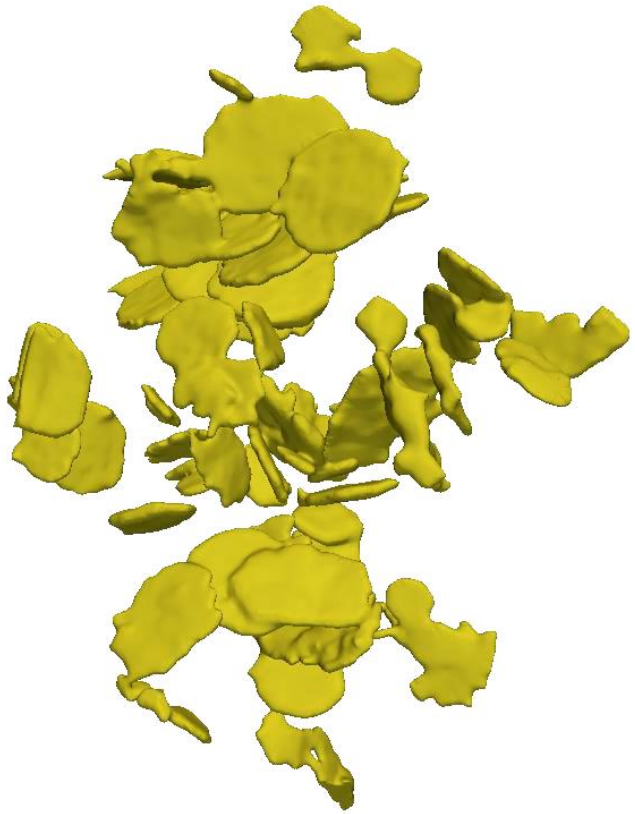
Ex. 1: **POLYMER NANOCOMPOSITES**
Dispersion of Mg_3AlCO_3 Layer-Double Hydroxide nanoplatelets in latex


Images 4K, 0.2 sec

step-by-step series,
+70 to -70°, 200 sec.
(pause 0.5 sec,
total electron dose
≈ 2.4 10^4 $e^-/Å^2$ *'validated' by an irradiation test*)



3D model (Mg_3AlCO_3 LDH nanoplatelets)



Thierry EPICIER, *Univ. Lyon*

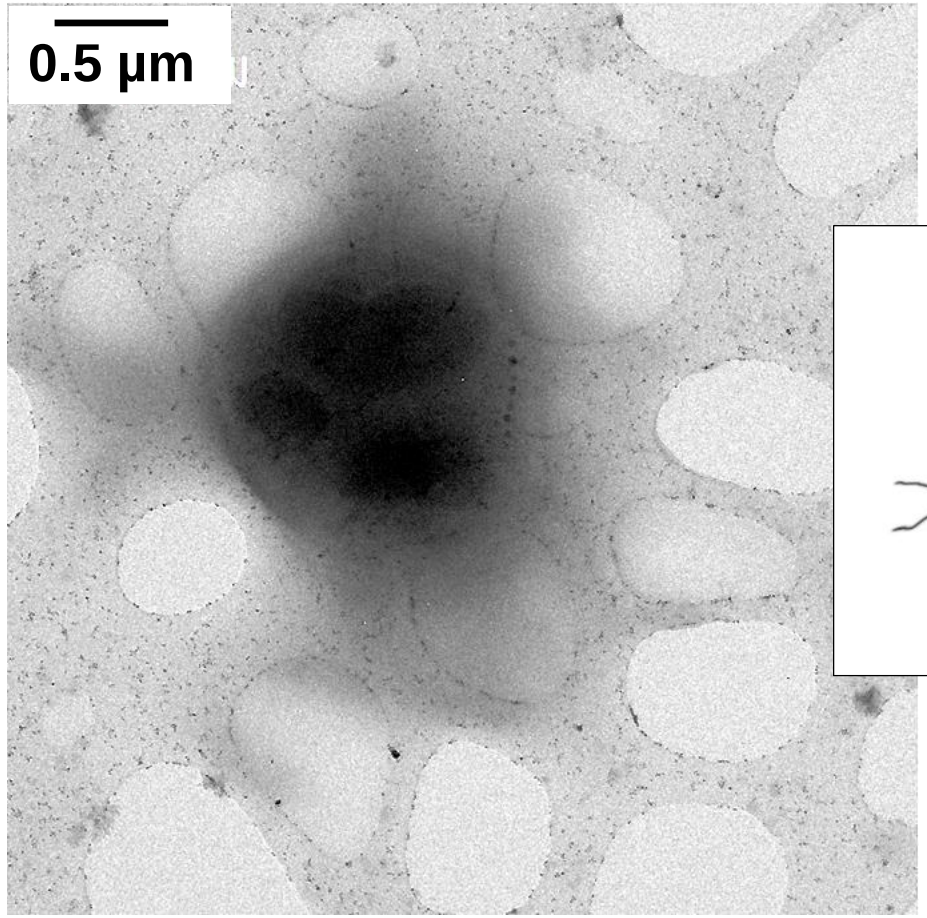
Some (ETEM) applications of fast tomography

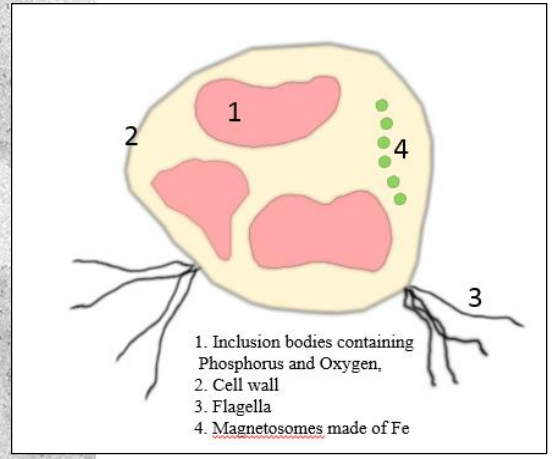
- **Fast tomography of electron beam sensitive materials**

Ex. 2: **BIOLOGICAL MATERIAL: Magnetotactic bacteria** R. BLAKEMORE, *Science* **190** (1975) 377–379

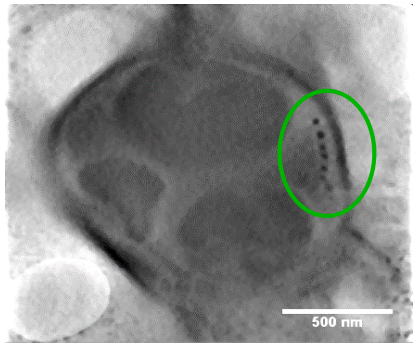
Images 1K, 0.2 sec

step-by-step series, -50 to 50°, 90 sec.
(pause 0.5 sec)





Slice from the 3D model

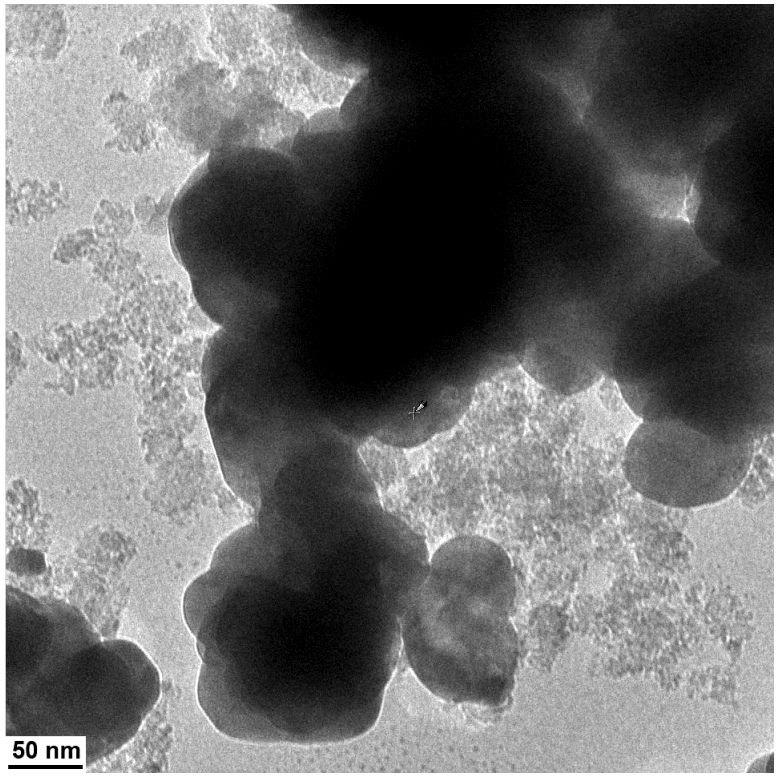


magnetosomes

Perspectives (and conclusions): 3D Operando ETEM

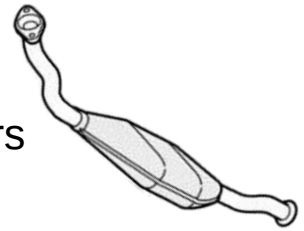
- ***COMBUSTION of SOOT on ZrO_2***

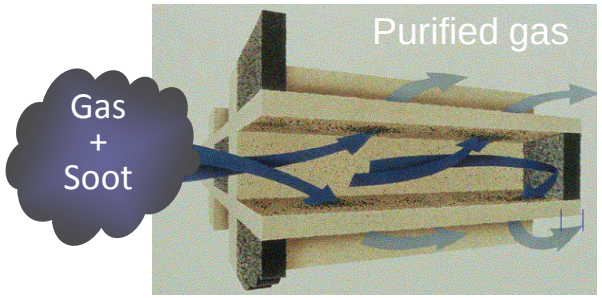
ETEM 80 kV, 500°C, 3 mbar O_2



Total time **3 min 05 sec** (speed x10)

from Oct. 2010:
Diesel **P**articulate **F**ilter
compulsory on Diesel cars

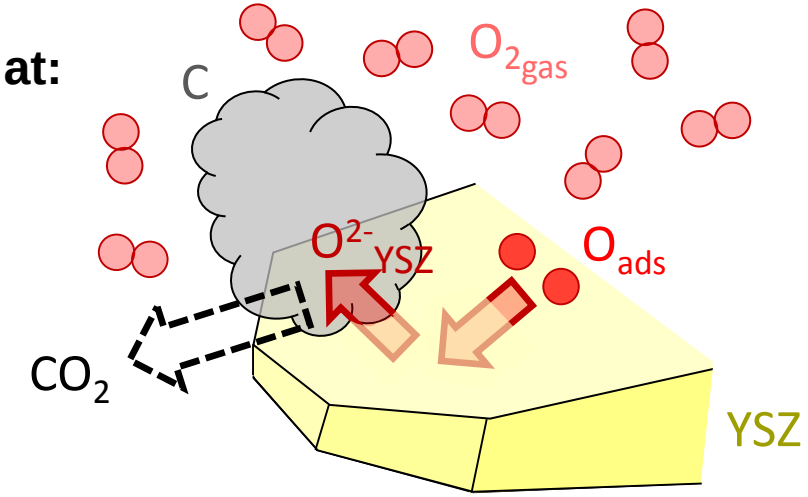




$C + 2\,O^{2-}_{YSZ} \rightarrow CO_2 + 4\,e^-$ (though the soot)

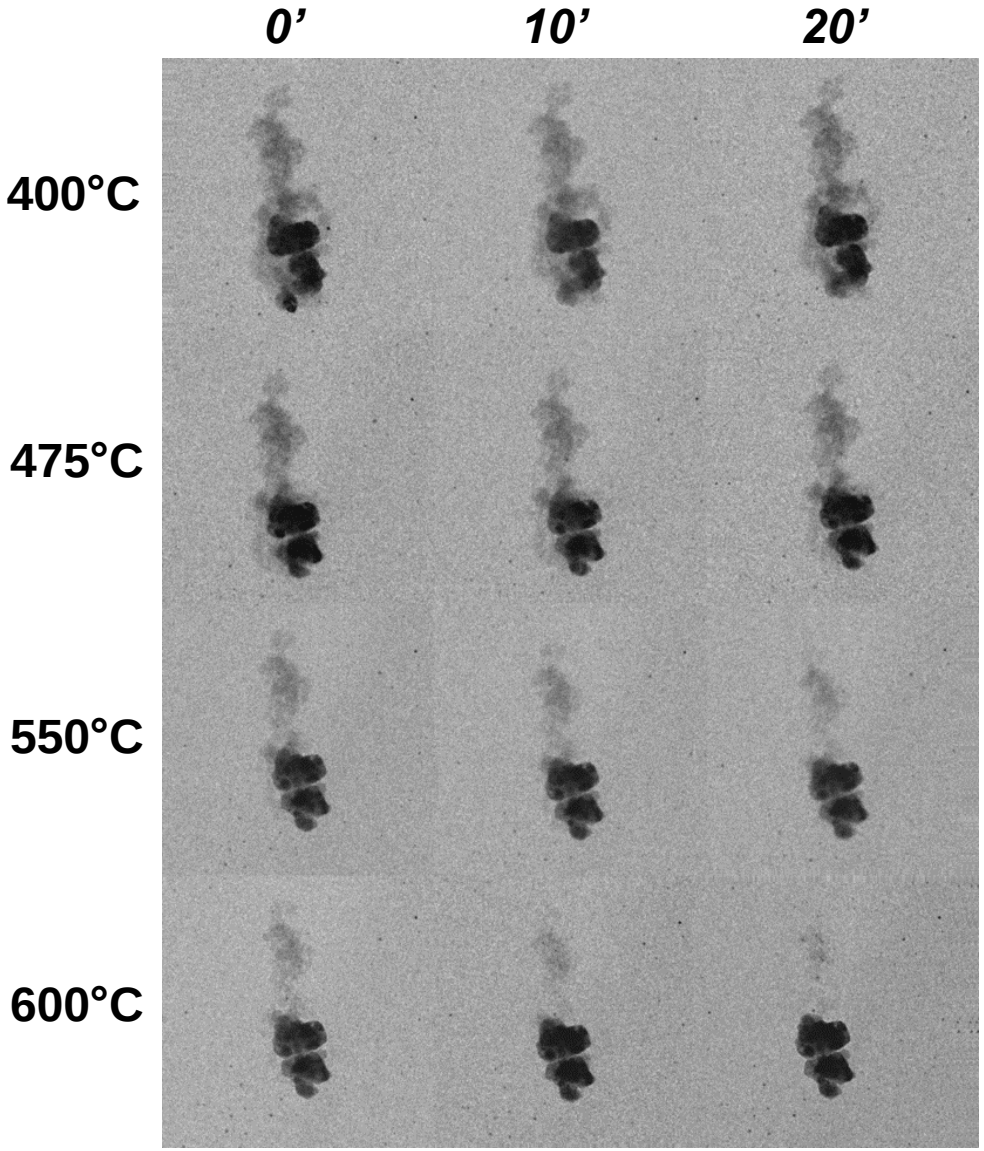
50% of soot conversion at:

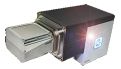
- 680°C without catalyst
- 520°C on YSZ



A. SERVE et al., *Applied Catal. A* **504** (2015) 74-80

Perspectives (and conclusions)**: 3D Operando ETEM**





Images 4K, 0.04 sec

Exposure time ≈ 2 h 45 min

flux 1.7 $e^{-}.Å^{-2}.s^{-1}$

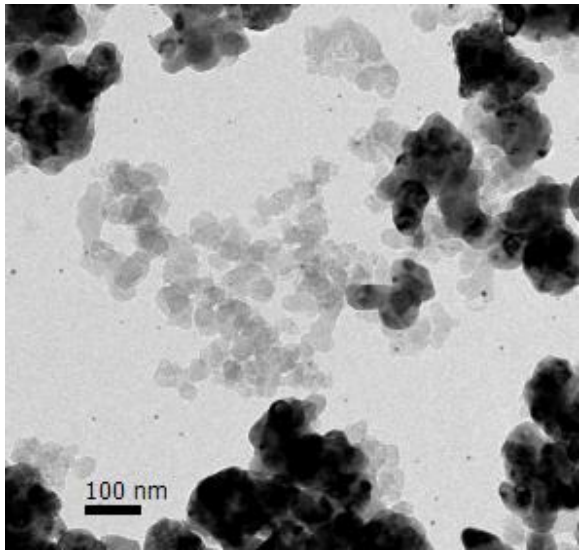
Total dose 1.7 10^{4} $e^{-}.Å^{-2}$

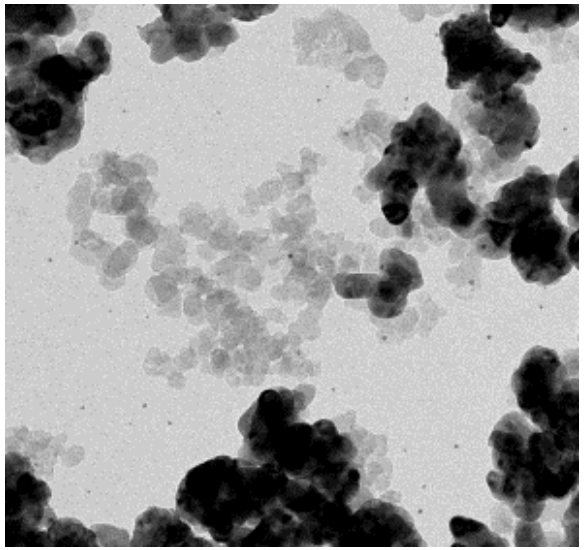
Irradiation test 5 min

flux 56 $e^{-}.Å^{-2}.s^{-1}$

Total dose 1.68 10^{4} $e^{-}.Å^{-2}$

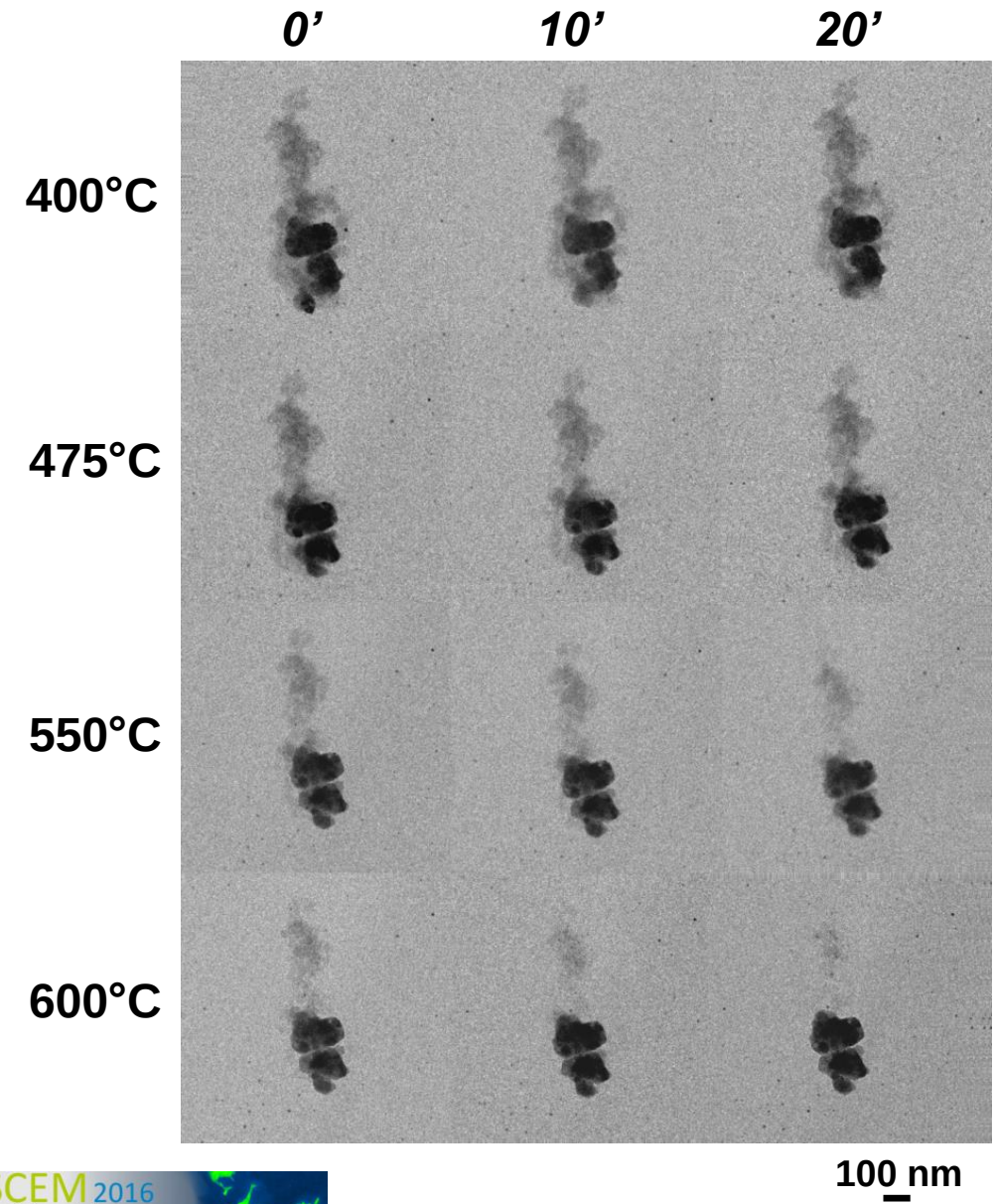
test start

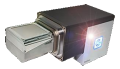




test end

Perspectives (and conclusions)**: 3D Operando ETEM**

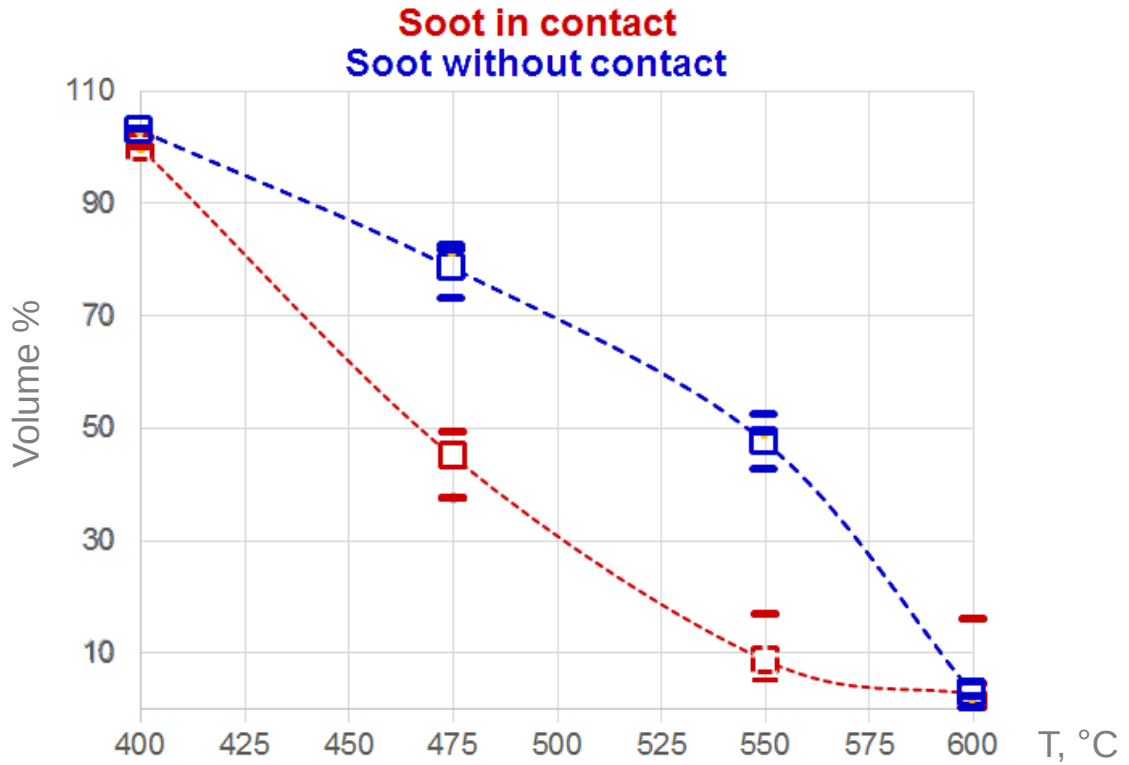




Images 4K, 0.04 sec

‘step-by-step’ series, +70° to -71° in 130 sec, one tilt series **every 5 min** under 1.7 mbar O_2 at **400°C**, 450°C, **475°C**, 500°C, 525°C, **550°C**, **600°C**

(Total 35 tilt series ≈ 2 h 45 min)



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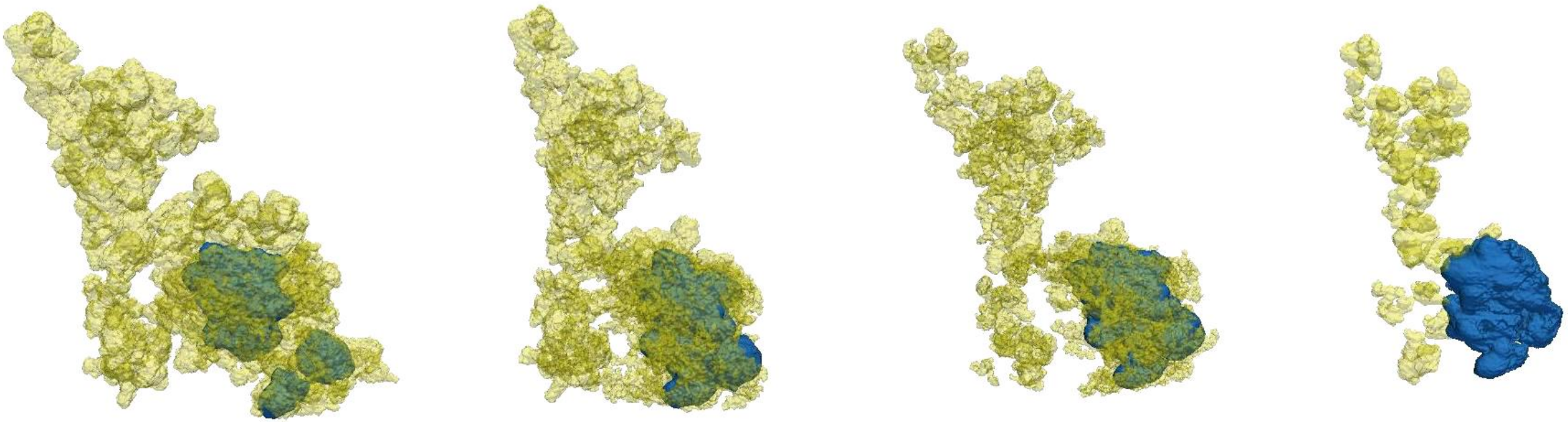
Perspectives (and conclusions)**: 3D Operando ETEM**

Time 0 sec at **400°C** **475°C** **550°C** **600°C**



100 nm

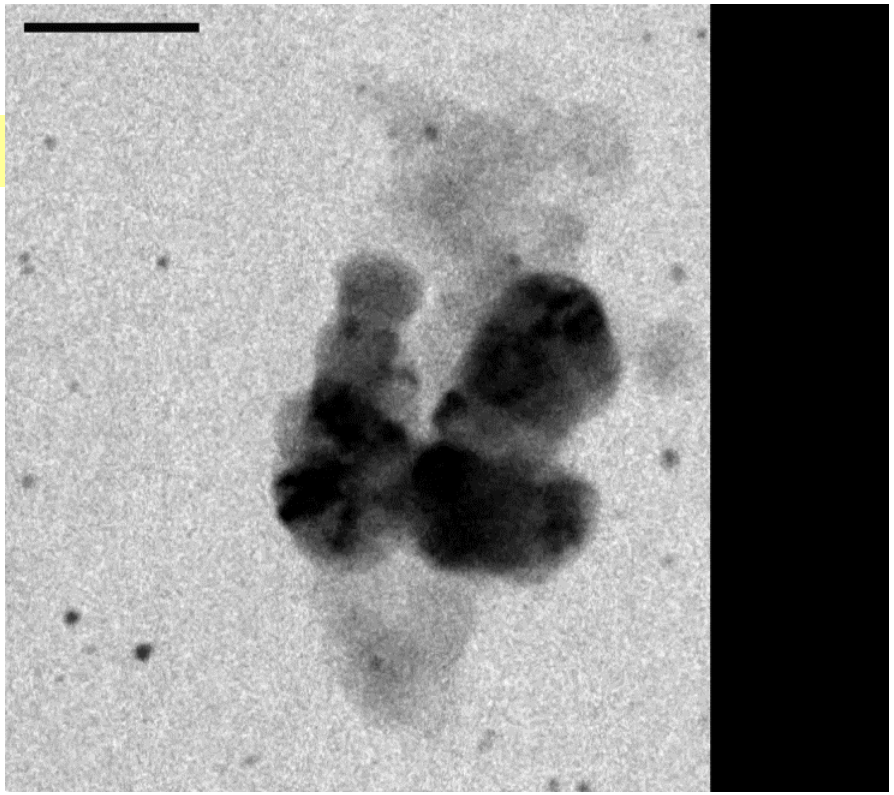
Soot **ZrO_2**

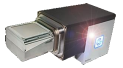
Perspectives (and conclusions): 3D Operando ETEM

- **REMINDER: *3D acquisition at the SECOND LEVEL***

Rotation angular amplitude: 2α	*140°*
Total acquisition time: t_{total}	*5 sec*
Angular rotation speed $\omega = 2\alpha/t$	*28°/sec*
Number of frames per second: ***Fps***	*100*
Angular blur / frame: $\mathbf{BIfr} = \frac{2\alpha}{t.Fps}$	*0.28°*

Oneview GATAN
2K, 100 images/sec




true speed,
100 fps, 2K images

tilt series +73°/-70° in ***5.1 sec*****, 5 10^{-5} mbar O_2, 300°C**

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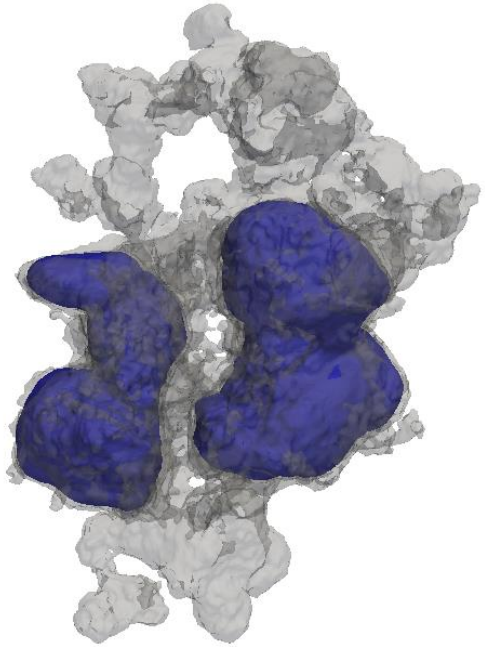
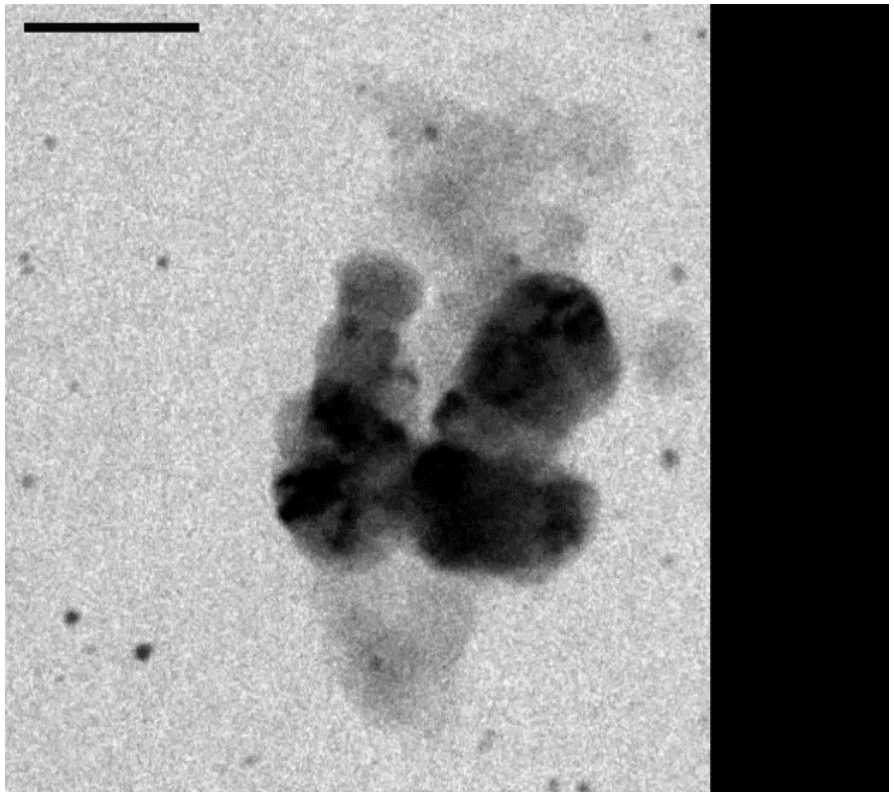
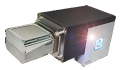
Perspectives (and conclusions)**: 3D Operando ETEM**

- **REMINDER:** ***3D acquisition at the SECOND LEVEL***



100 nm





true speed,
100 fps, 2K images

tilt series +73°/-70° in ***5.1 sec*****, 5 10^{-5} mbar O_2, 300°C**

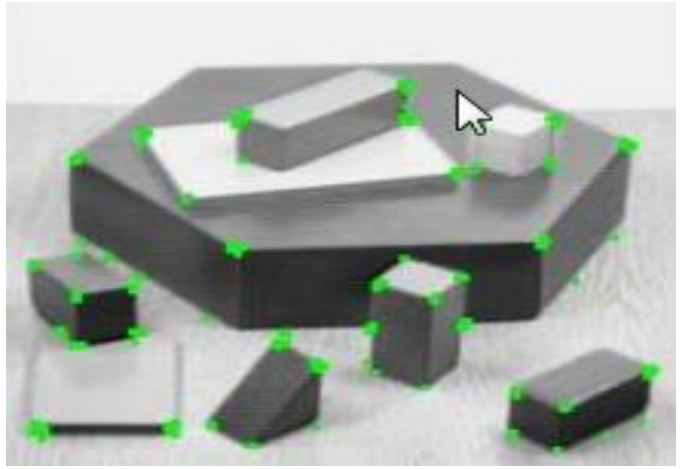
Perspectives (and conclusions): 3D Operando ETEM

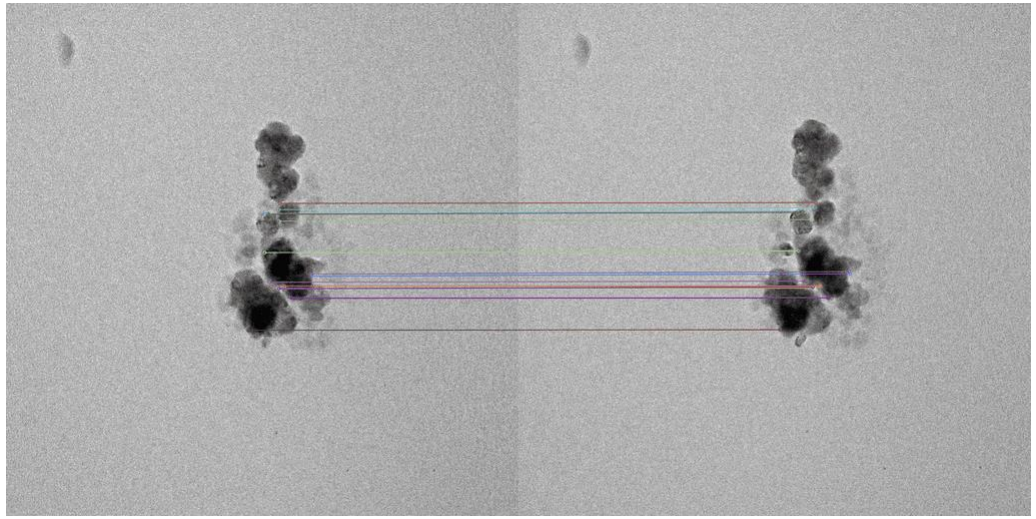
- **Further improvements** *(running ANR project)*

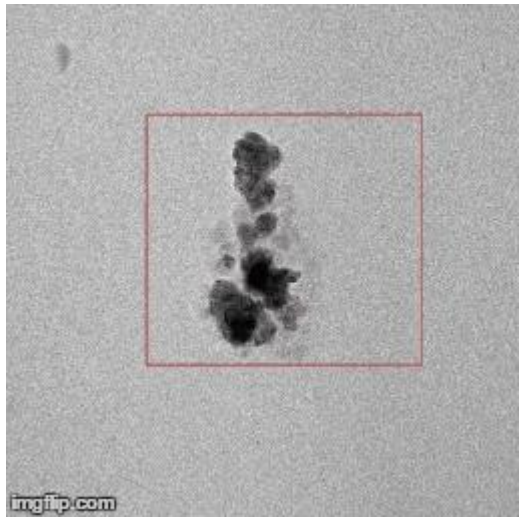
1) Live 'alignment'

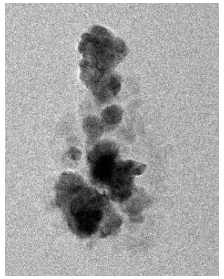
Local descriptors

- **SIFT** (**S**cale **I**nvariant **F**eature **T**ransform)
- **SURF** (**S**peeded **U**p **R**obust **F**eatures)
- **ORB** (**O**riented FAST and **R**otated **B**RIEF)









Soot on ZrO_2
1.7 mbar O_2, **400°C**
Post-mortem alignment, 0.25 sec/image

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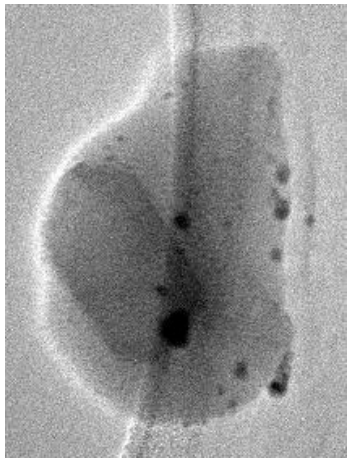
Perspectives (and conclusions): 3D Operando ETEM

- **Further improvements** *(running ANR project)*

2) 'Deblurring'

sharp image S



Pd nanocatalysts supported on αAl_2O_3

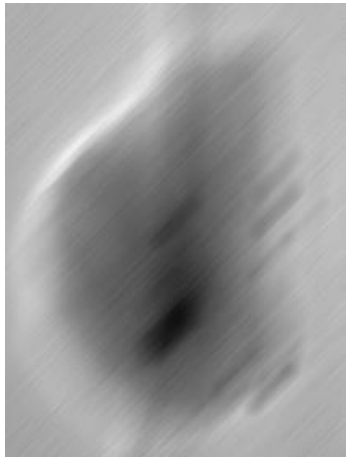
$$B = S \otimes F + n$$

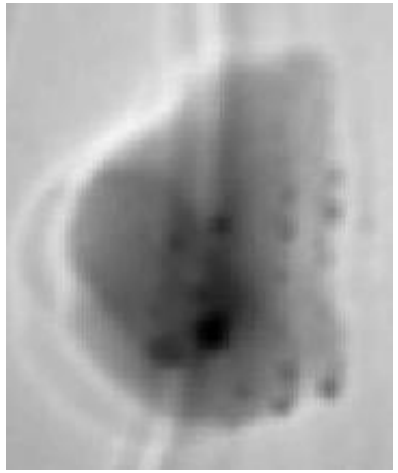
Convolution

Example 1: drift ***F***

Example 2: displacement

Blurred image B



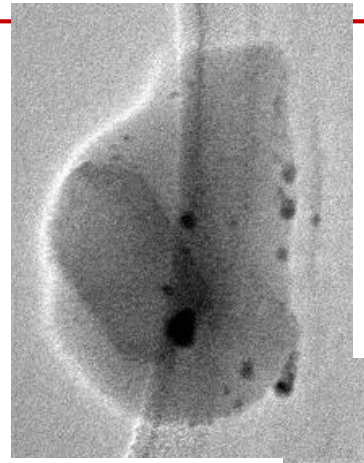


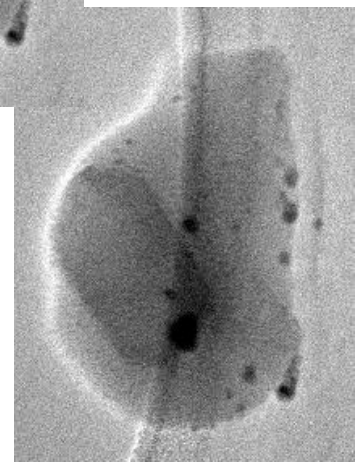
Deconvolution filtering

Wiener

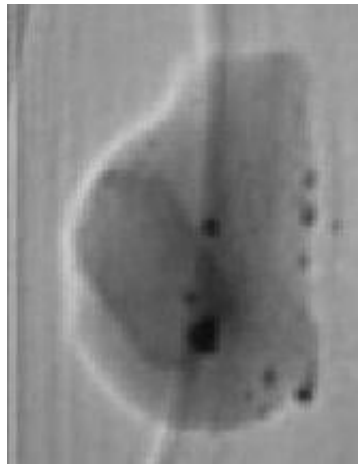
Constrained **L**east **S**quares

Fast **I**terative **S**hrinkage / **T**hresholding **A**lgorithm

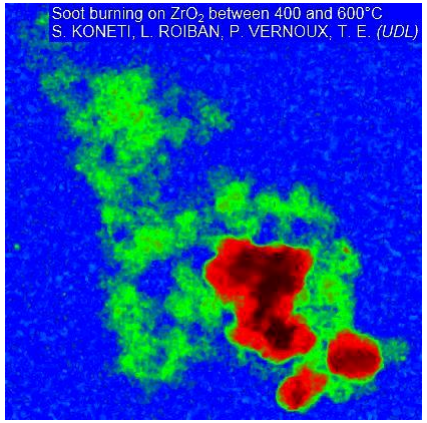




Estimated images S_E



ACKNOWLEDGEMENTS



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