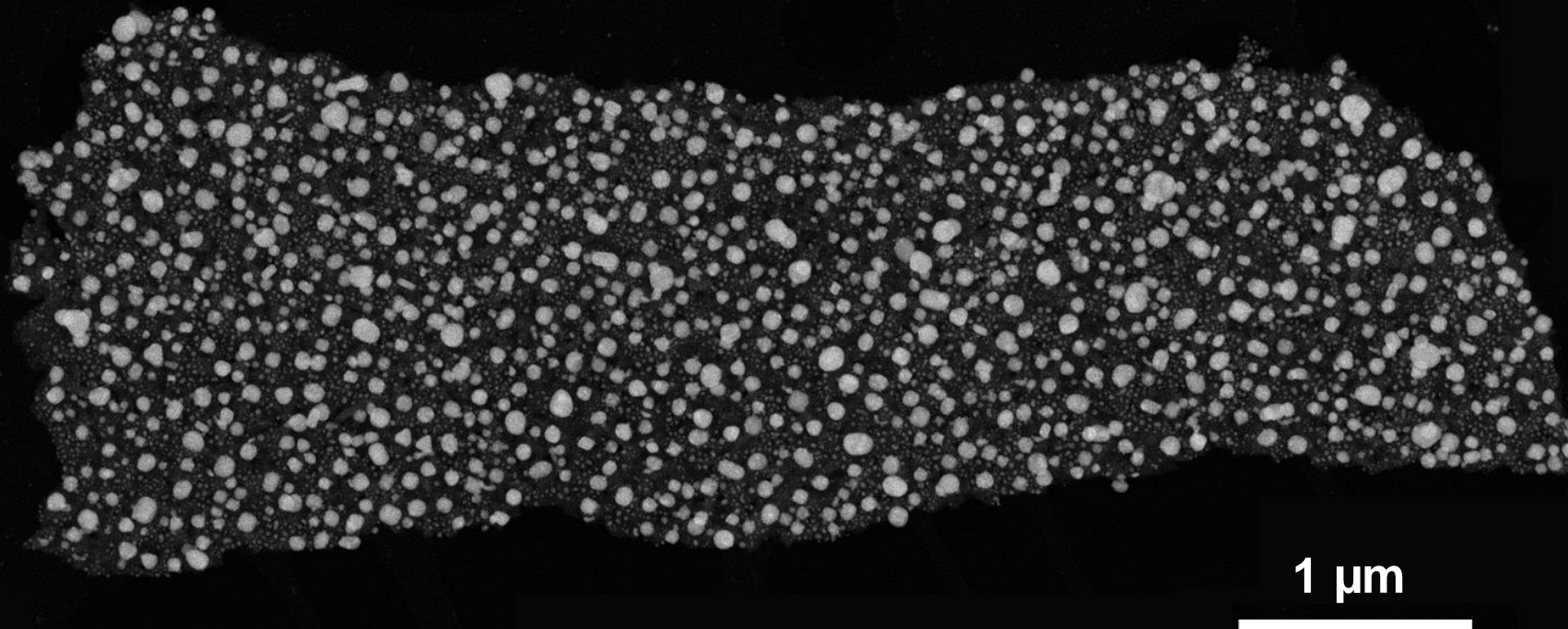
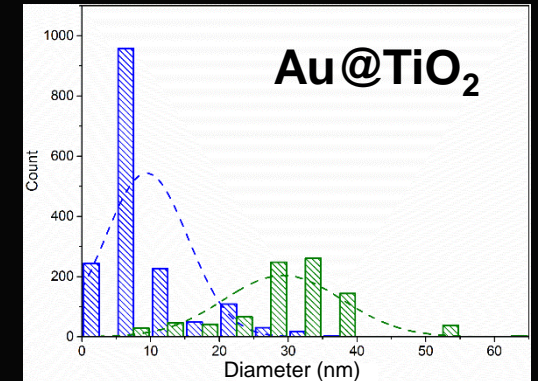


Apports de la MET et de la microscopie électronique avancée environnementale à l'étude de nanoparticules (multi-)fonctionnelles



S. KONETI et al., *in progress*

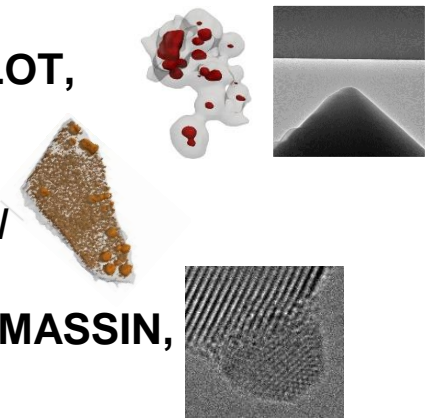


Thierry EPICIER

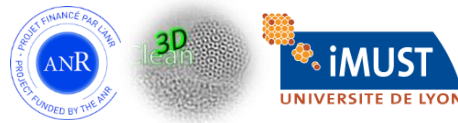
University of Lyon / INSA de Lyon, MATEIS, umr CNRS 5510, Villeurbanne, FRANCE

ACKNOWLEDGEMENTS

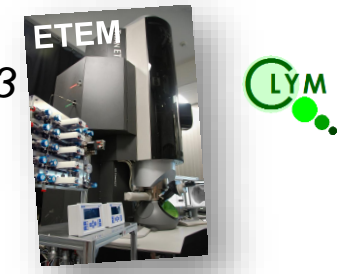
- Sid KONETI, Lucian ROIBAN, Philippe STEYER, L. JOLY-POTTUZ, K. MASENELLI-VARLOT, Florent DALMAS, *MATEIS INSA-Lyon*, Anne-Sophie GAY, *IFPen*
- Joel BORGES, Marco S. RODRIGUES, Felipe VAZ, *Universidade do Minho, Braga, Portugal*
- Mimoun AOUINE, Francisco J. CADETE SANTOS AIRES, Philippe VERNOUX, Laurence MASSIN, Patrick GELIN, *IRCELYON, University Lyon I*
- Florent TOURNUS, *ILM, University Lyon I*, Kazuhisa SATO, Toyohiko KONNO, *IMR, Sendai-Japan*, P.H. JOUNEAU, P. BAYLE-GUILLEMAUD, *CEA-Minatec Grenoble*



- ANR project '3DCLEAN' n°15-CE09-0009-01, LabeX 'IMUST' Université de Lyon (ANR)





- CPER 2007-2013



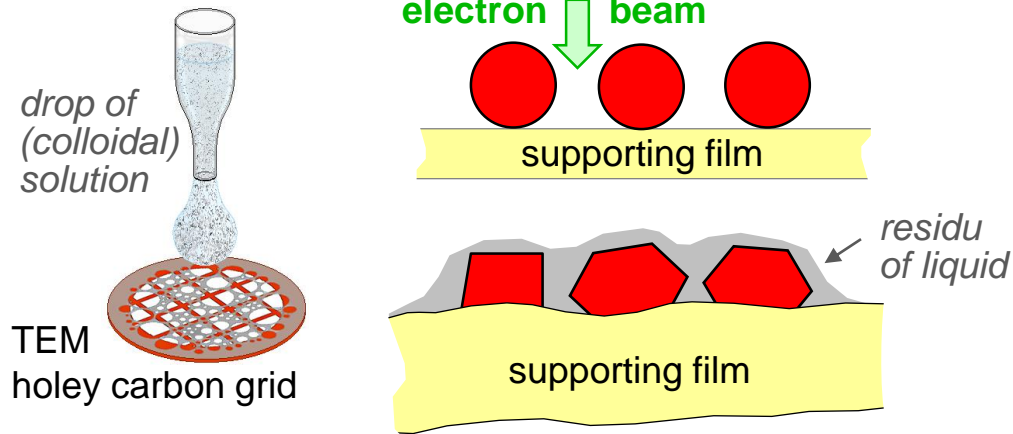
- www.metsa.fr



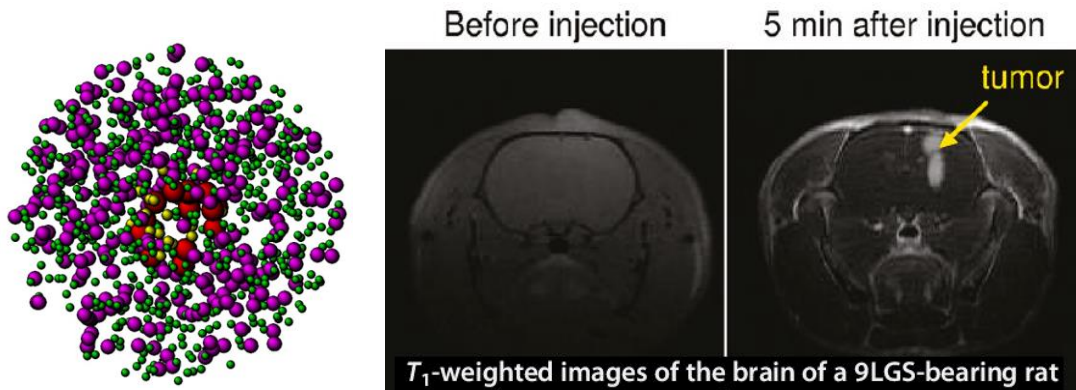
Microscopie Électronique en Transmission et Sonde Atomique
I.R. FR 3507  
DU : Mathieu KOCIAK, LPS, kociak@lps.u-psud.fr
DUA : T. EPICIER

Note: this pictogram in the next slides marks videos in the original presentation

NPs in the TEM



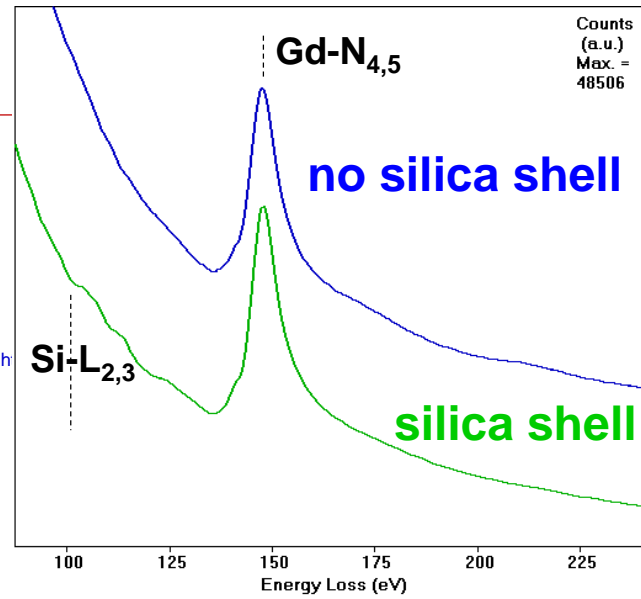
An example:
 theranostic $Gd_2O_3@SiO_2$ core-shell NPs



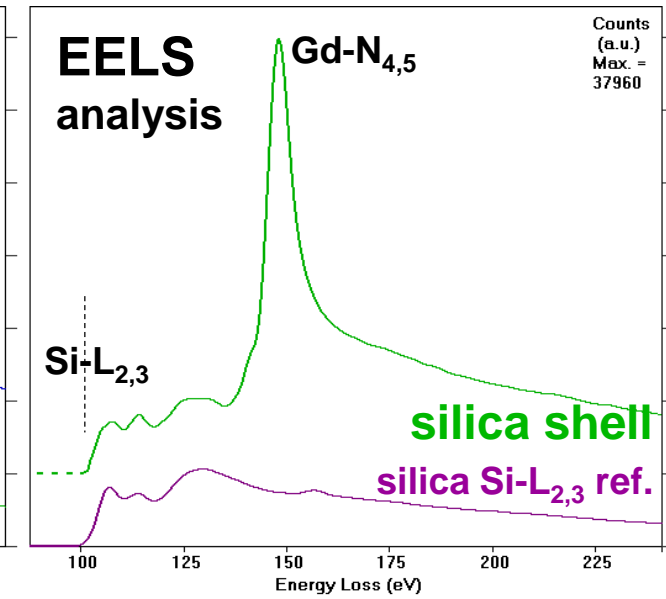
SiO_2 shell ≈ 1 nm (thickness)
 Gd_2O_3 core ≈ 1 nm

JEOL 2010F

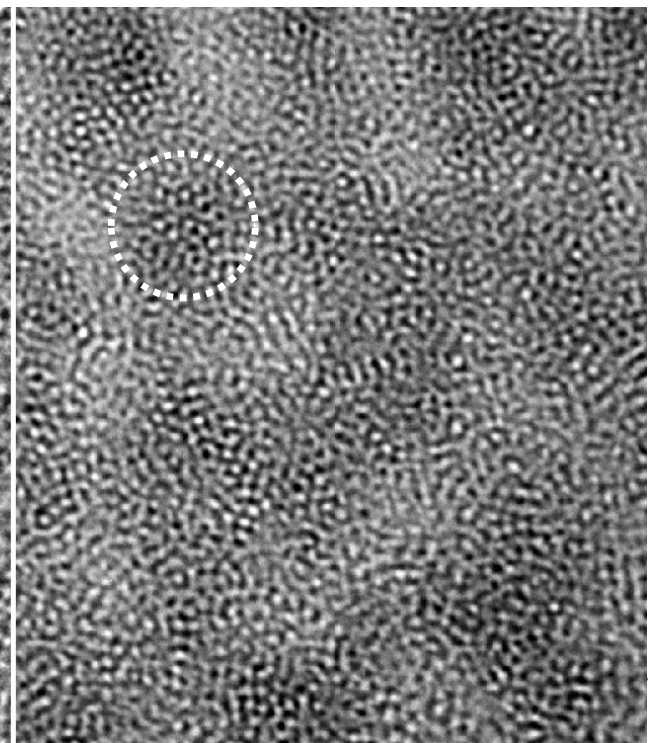
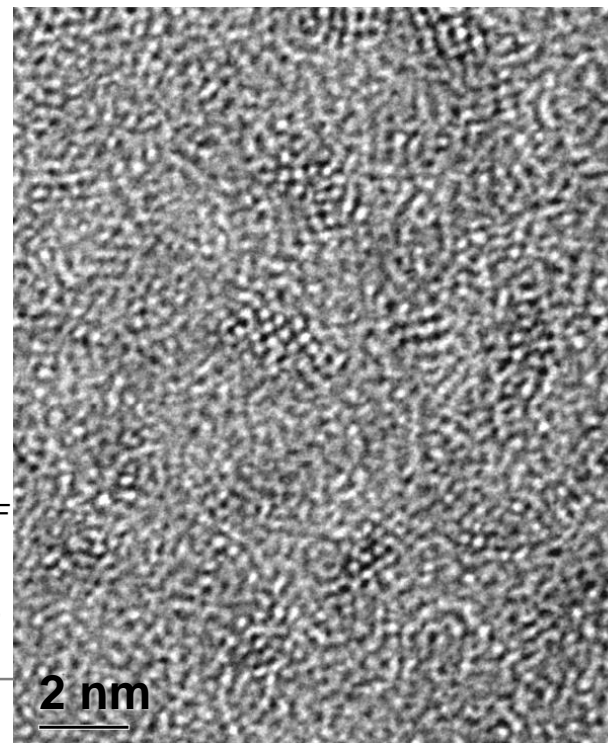
G. LE DUC et al., *ACS Nano*, **5** 12 (2011), 9566



1 nm Gd_2O_3 NPs

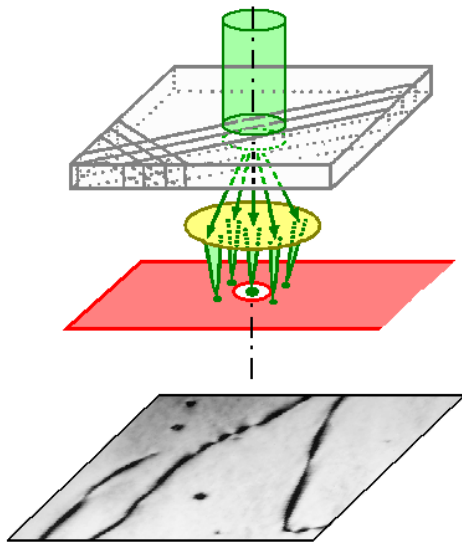


Core-shell $Gd_2O_3@SiO_2$

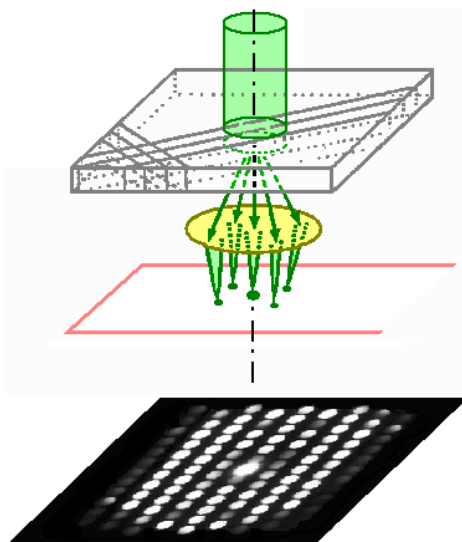


Main imaging techniques in the TEM

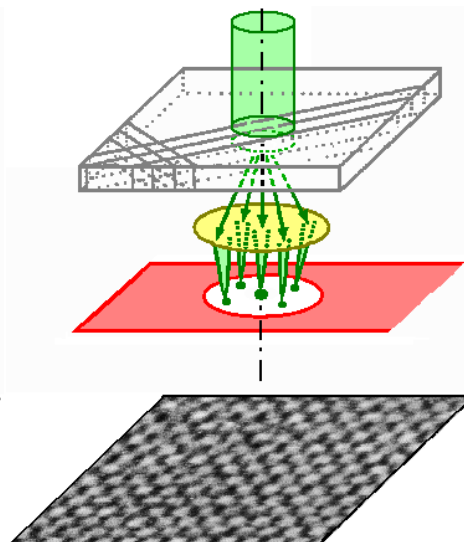
Conventional TEM + EDX



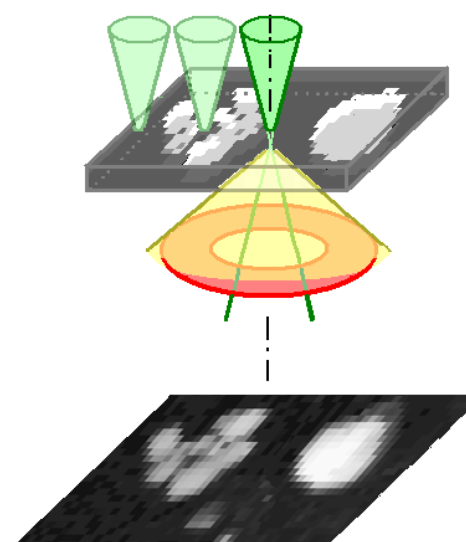
Electron Diffraction



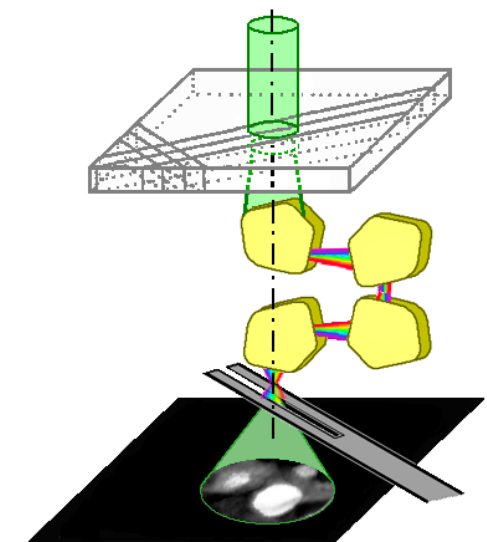
High Resolution TEM (HRTEM)



High Angle Annular Dark Field (HAADF) (Scanning TEM)



Energy Filtered TEM (EFTEM / EELS)



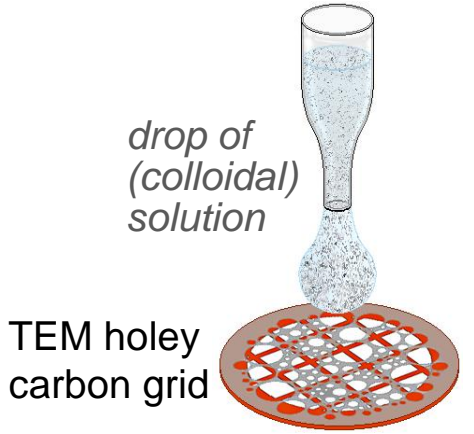
HIGH RESOLUTION imaging for *very small* NPs (< 5 nm)

ATOMIC RESOLUTION in CRYSTALS DOWN TO 0.1 nm
 - *information limit* with a Field Emission Gun
 - *true resolution* with a C_s -corrector

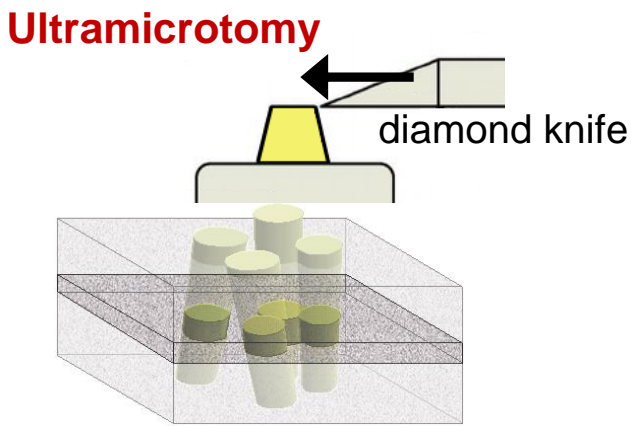
ATOMIC RESOLUTION BELOW 0.1 nm
 probe C_s -corrected machines

TEM sample preparation

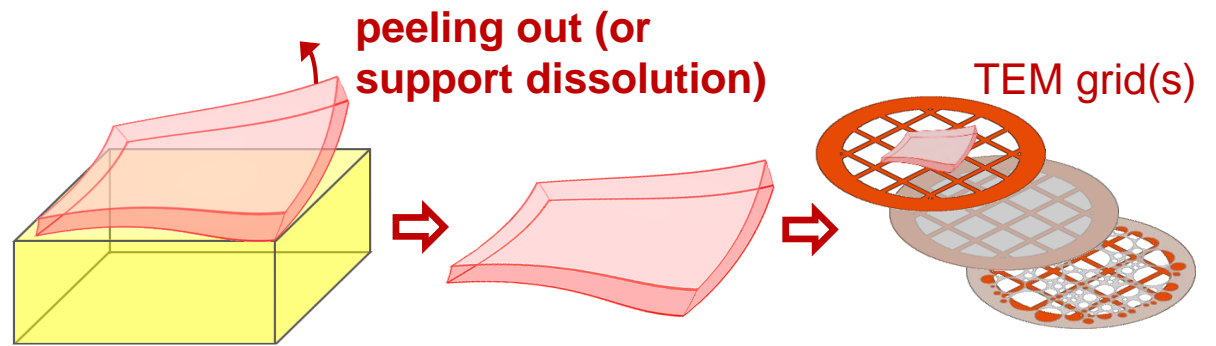
• NPs in a solution



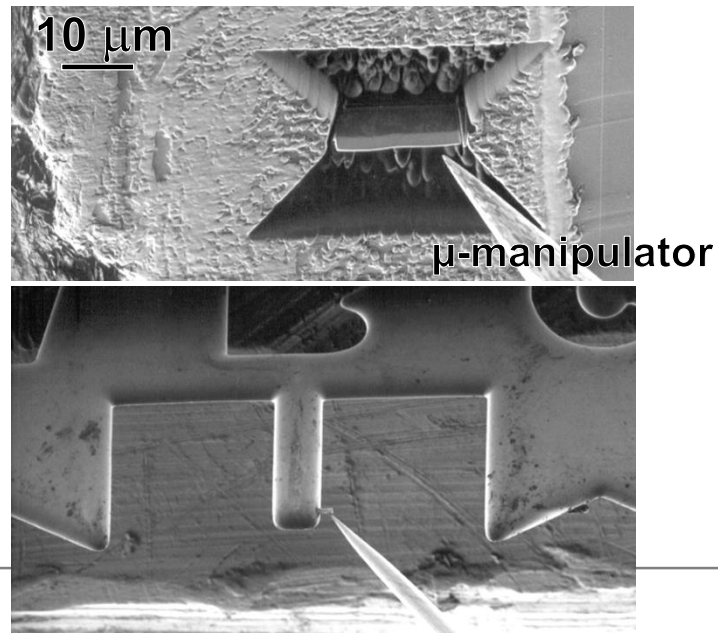
• NPs in a *solid* matrix



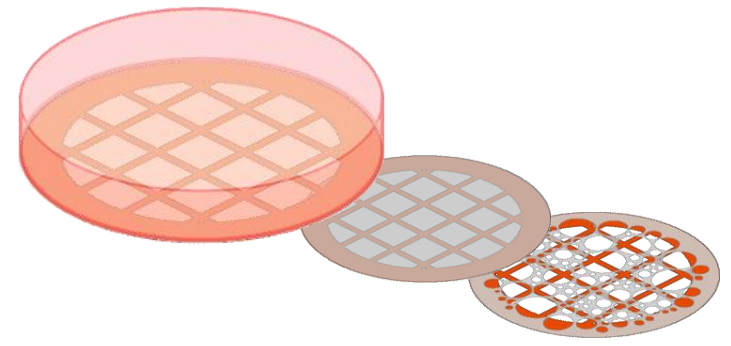
• NPs in a thin film



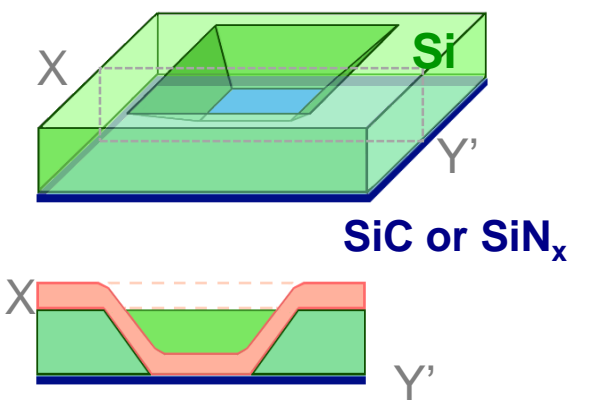
• NPs in a *solid* matrix (thin foils)



• Direct (single or co-) deposition on TEM supports



MEMS-based nanochip for heating (1300°C)

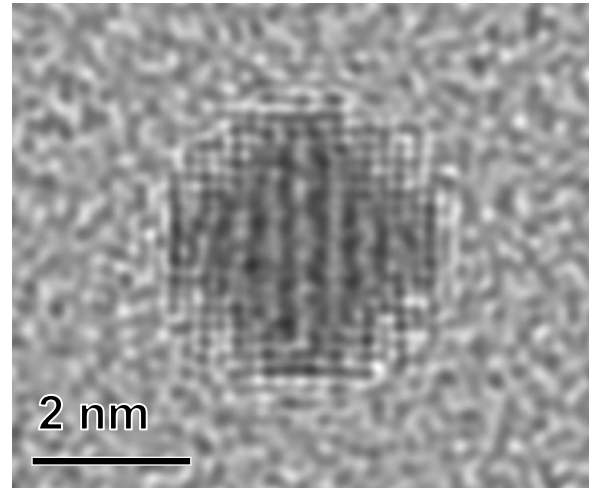


Aberration corrected HRTEM

Contrast Transfer Function

300 kV, $C_s = 1.2 \text{ mm}$ ($\Delta = 4.0 \text{ nm}$, $\theta_c = 0.2 \text{ mRad}$)

ordered FePt L1₀
(NP on C film)



$\delta f = -54 \text{ nm}$

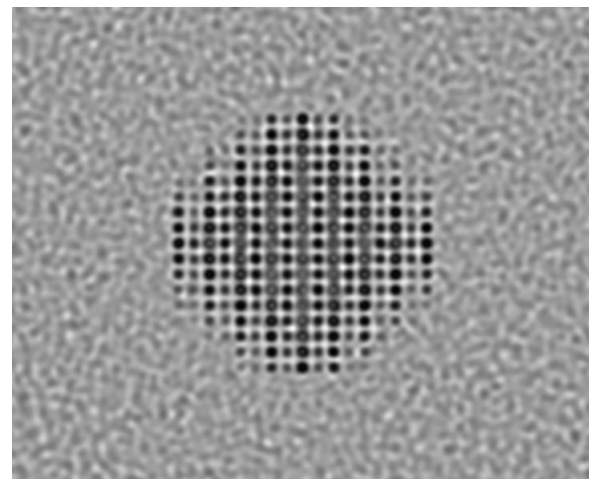
smaller underfocus



less Fresnel contrast



no delocalization



$\delta f = -6 \text{ nm}$

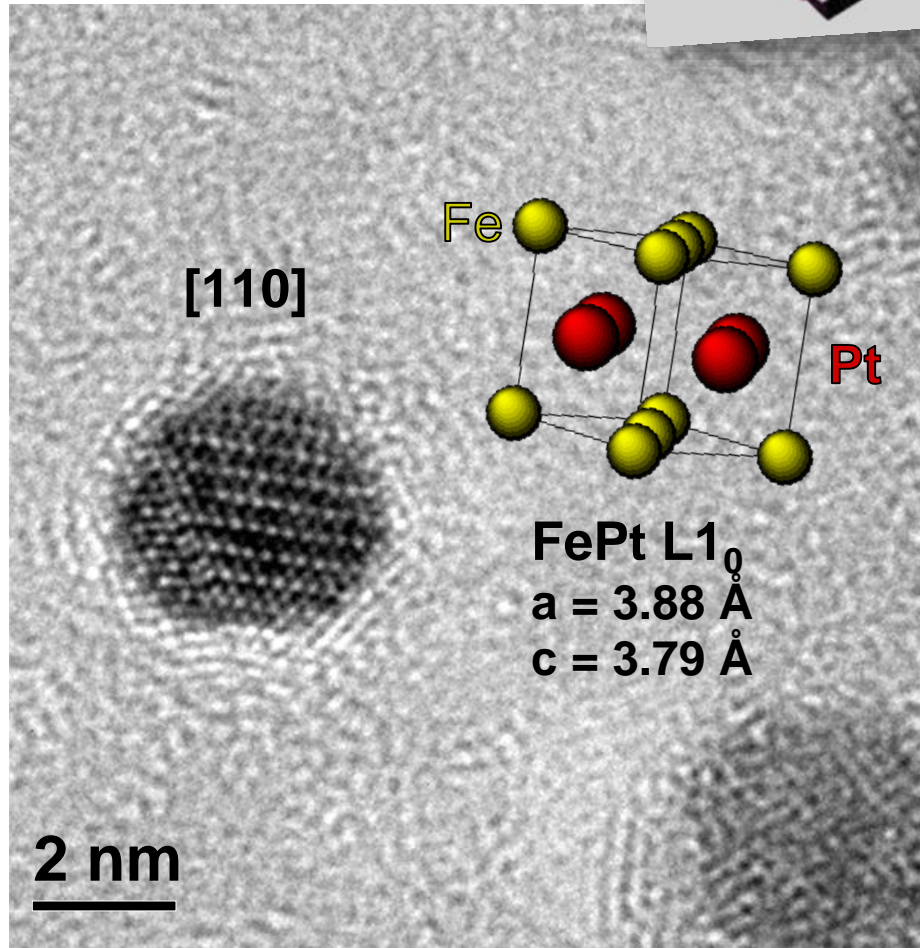
*simulations (JEMS,
© P. STADELMANN)*

300 kV, $C_s = 5 \mu\text{m}$ ($\Delta = 4.0 \text{ nm}$, $\theta_c = 0.2 \text{ mRad}$)

uncorrected JEOL 2010F

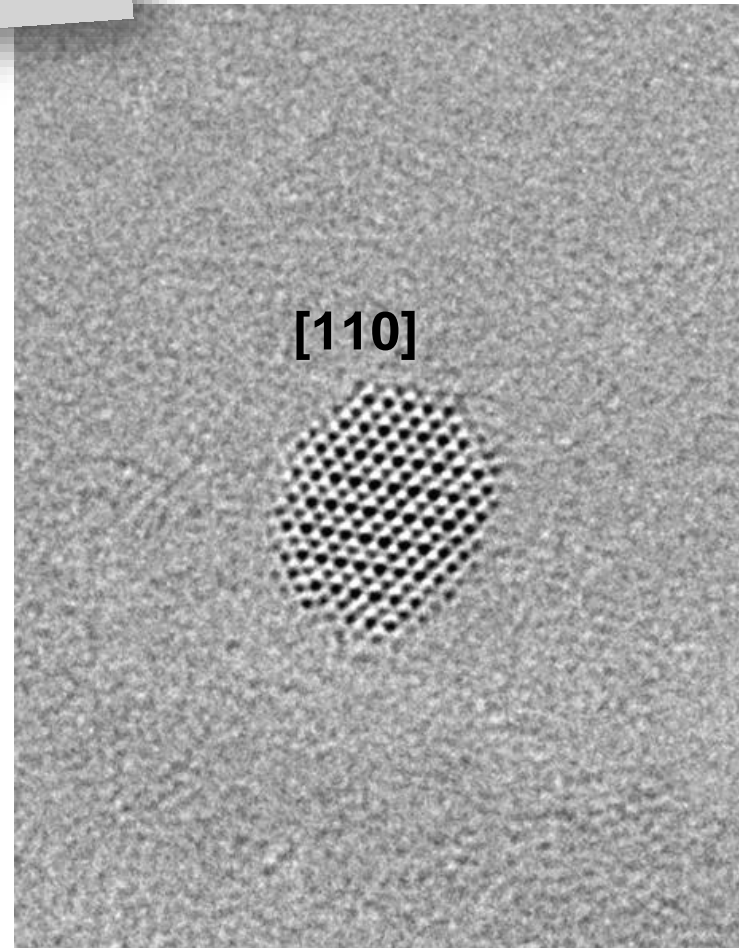


$C_s = 0.5 \text{ mm}, 200 \text{ kV}$

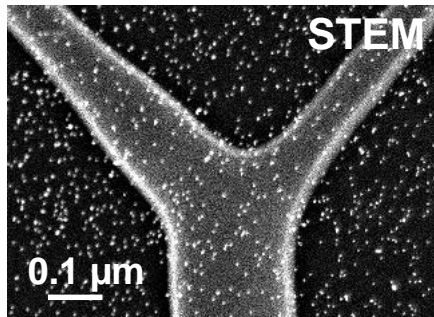


C_s corrected FEI Titan

$C_s = 1.4 \text{ \mu m}, 300 \text{ kV}$



Population of NPs deposited by Low Energy Cluster Beam Deposition (TEM grid)



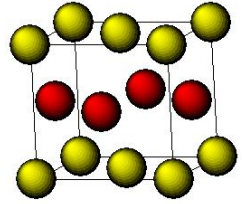
F. TOURNUS et al., *Phys. Rev. B* **77** (2008) 144411

C_s correction: BETTER RESOLUTION, sharper contrast, NO delocalization (Fresnel) EFFECTS

C_s corrected FEI Titan



fcc / L1₀ crystal

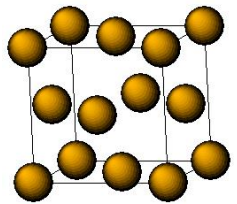


tetragonal L1₀
 $a_{\text{bulk}} = 0.379 \text{ nm}$
 $c_{\text{bulk}} = 0.367 \text{ nm}$

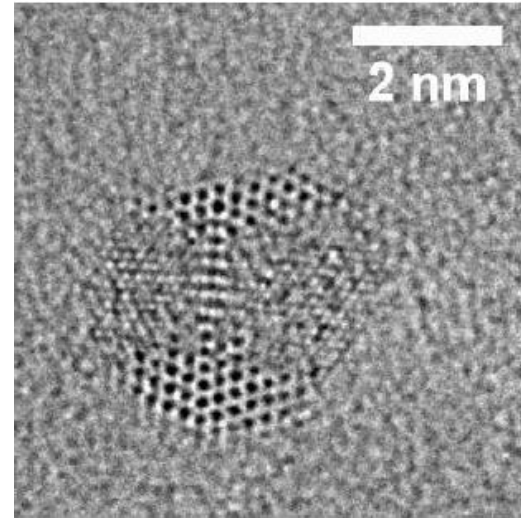
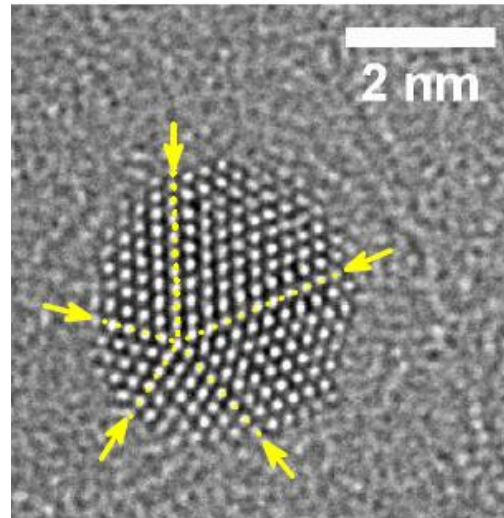
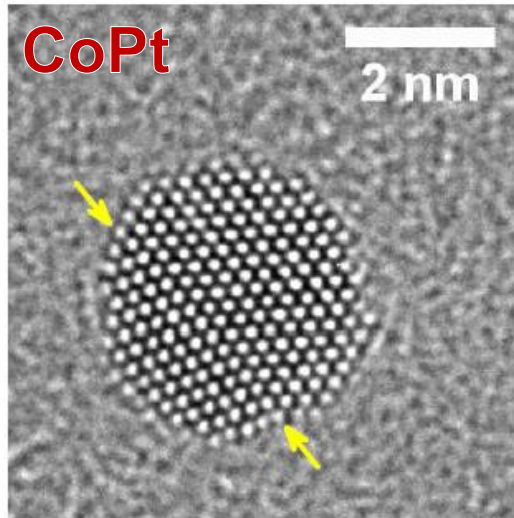
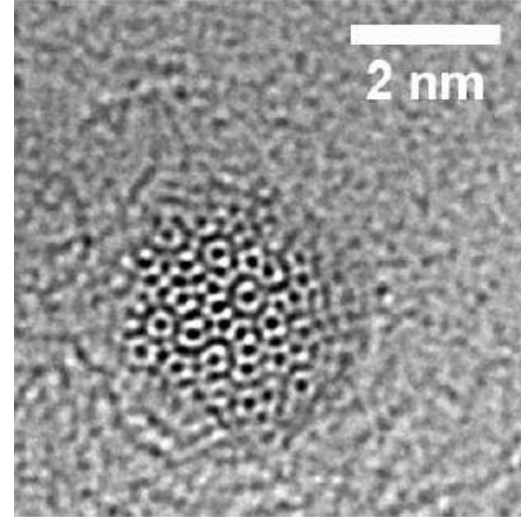
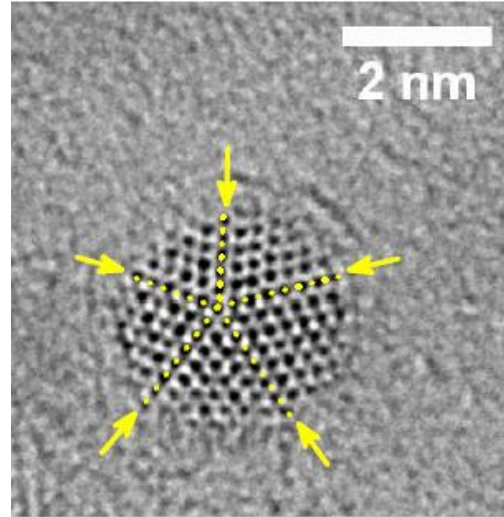
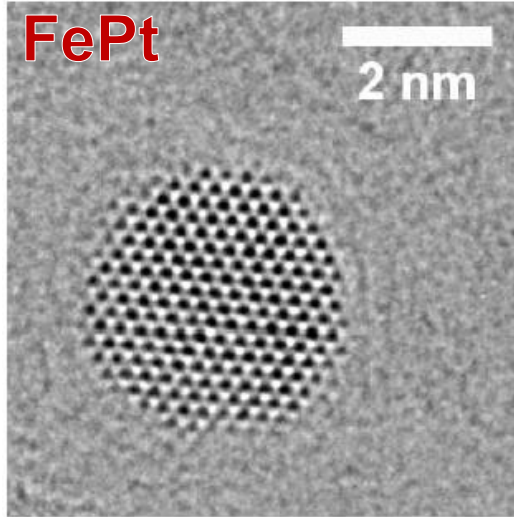
magnetic anisotropy

$EAL_{1_0} \approx 5 \text{ mJ/m}^3$

$\gg EA_{\text{fcc}} \approx 0.06 \text{ mJ/m}^3$

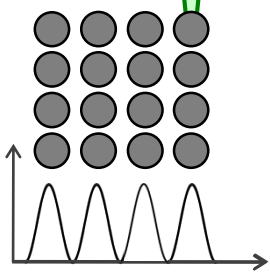


cubic fcc A1
 $a_{\text{bulk}} = 0.375 \text{ nm}$

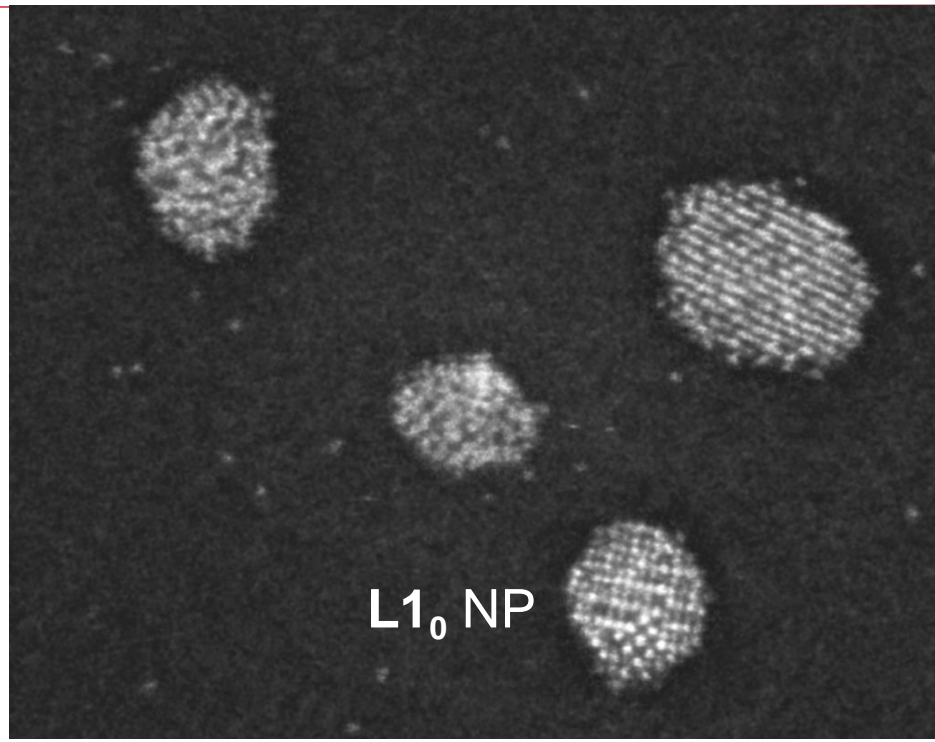
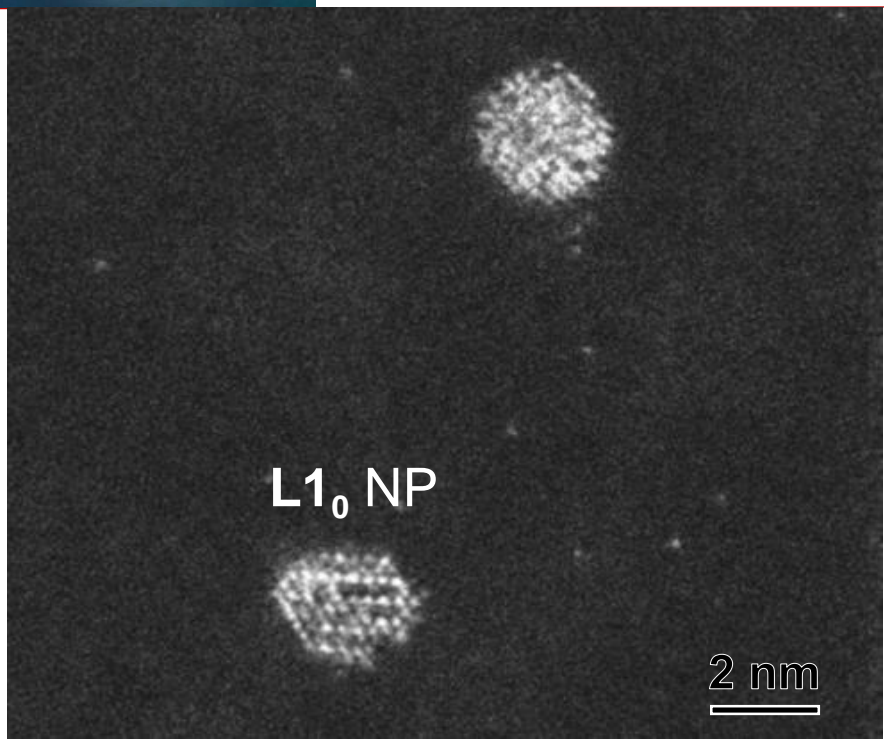


Aberration corrected HRSTEM

sub-Angström probe



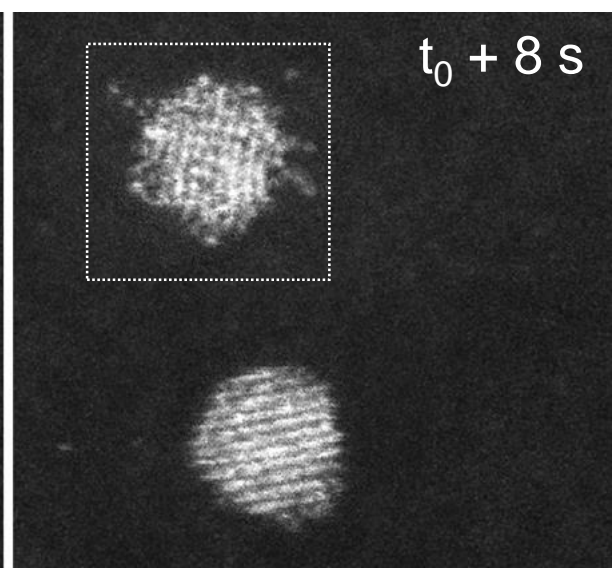
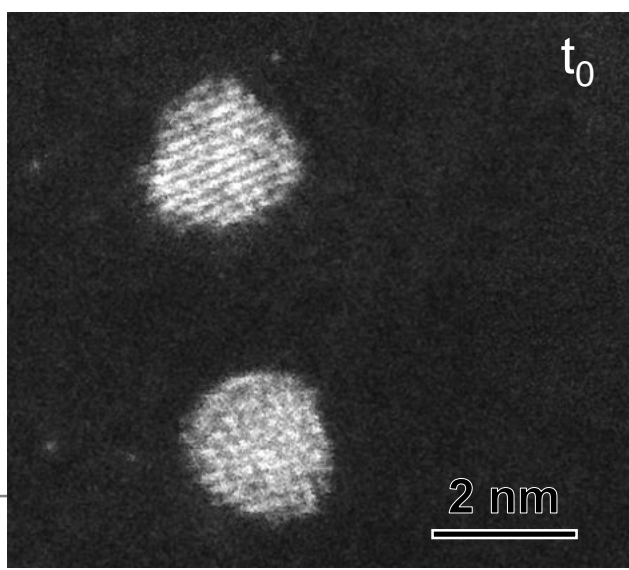
High
 Angle
 Dark-
 Field



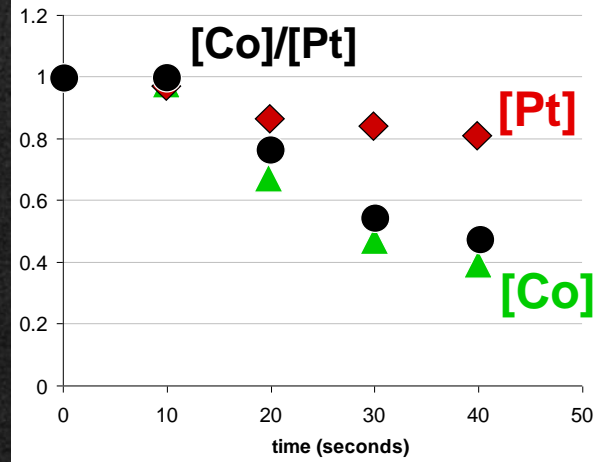
C_s corrected
 FEI Titan

300 kV

Minatec Grenoble
 P. BAYLE-G. et al.

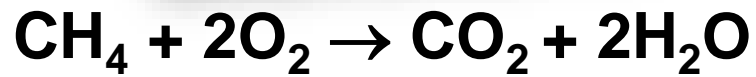
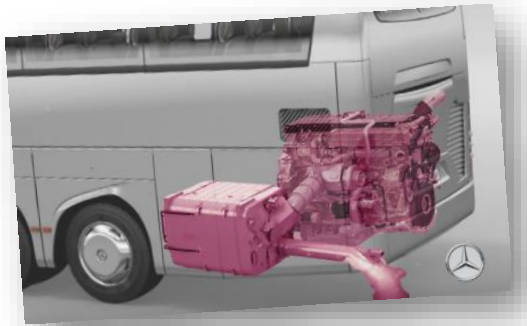


EDX, 3 nm nano-probe (JEOL2010F)

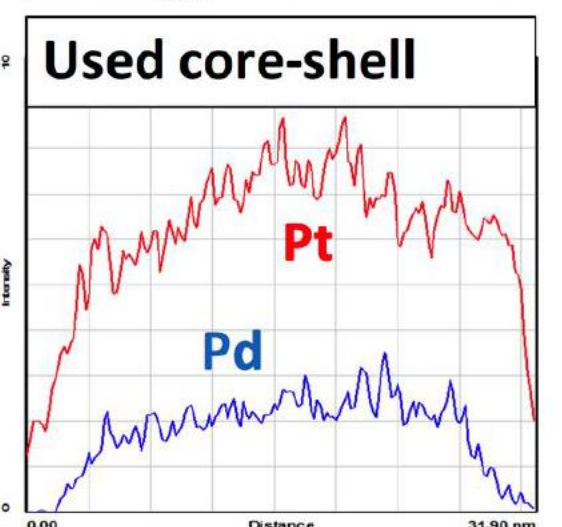
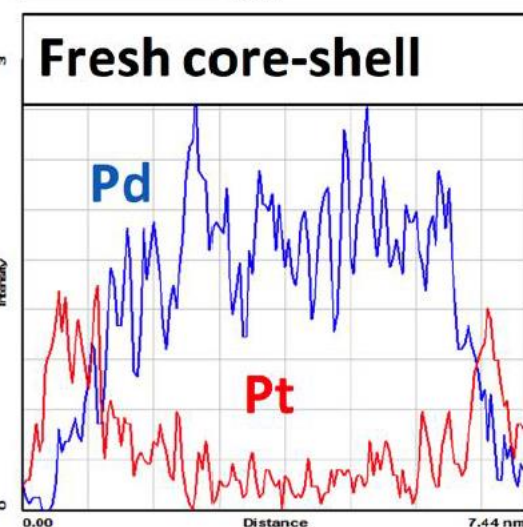
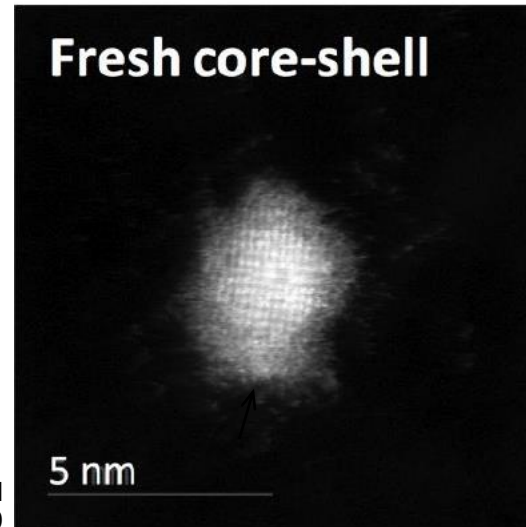
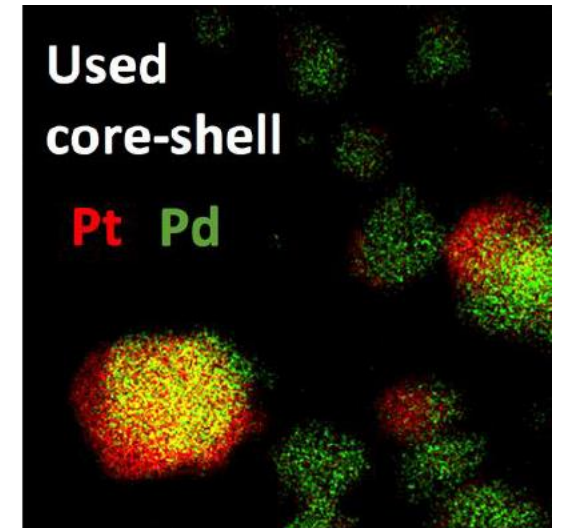
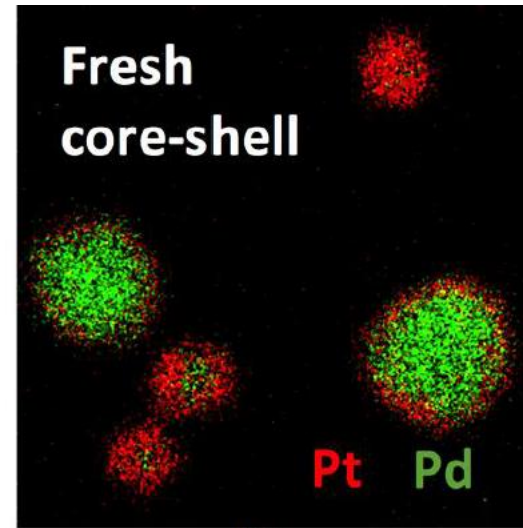
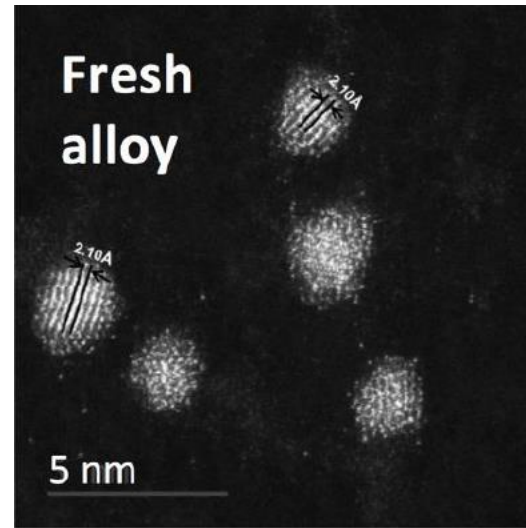


Aberration corrected HRSTEM

Pt-Pd catalysts for methane combustion



SDD EDX + Probe Cs-corrected
 Cold-FEG JEOL ARM200

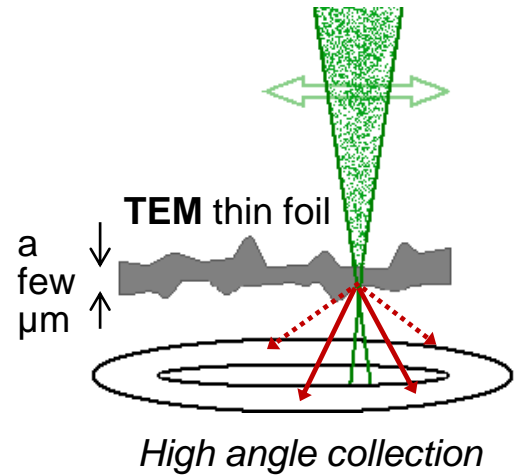


H. NASSIRI et al., *Chem. Engineer. Science* (2018)

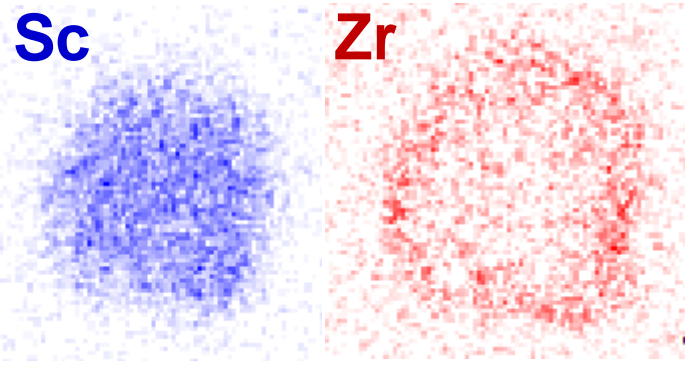
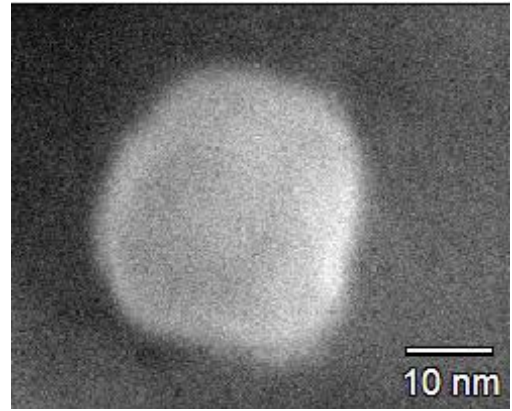
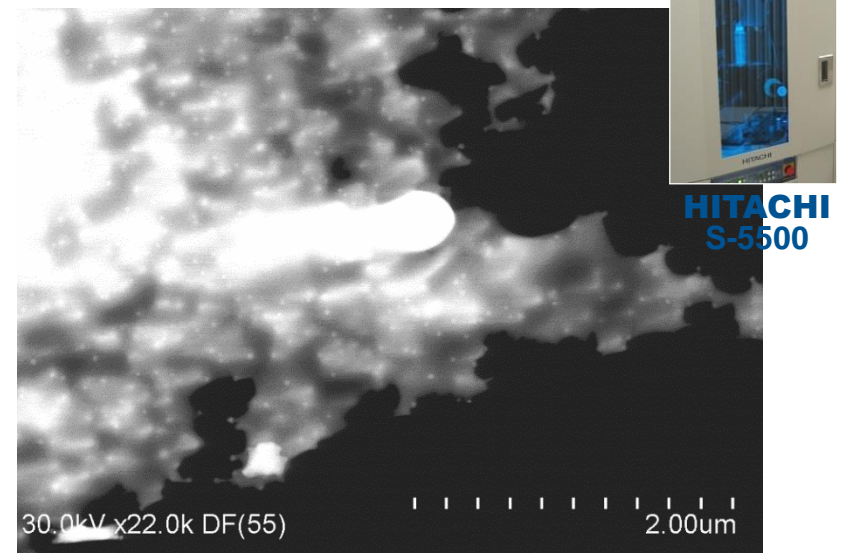
'Low voltage' STEM in Scanning Electron Microscopy

FEI XL30 30 kV

'HAADF-like' STEM mode

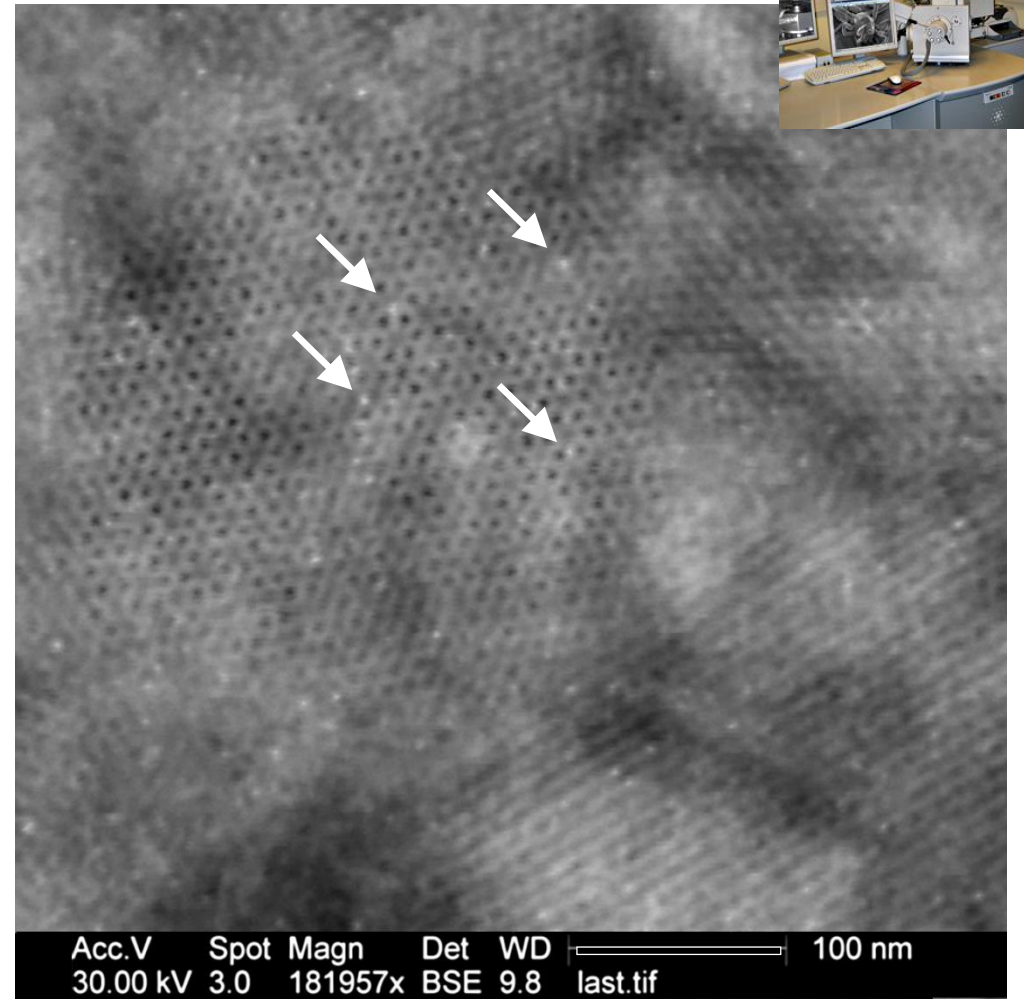


nanometric core-shell Al₃ZrSc precipitates in an Al alloy



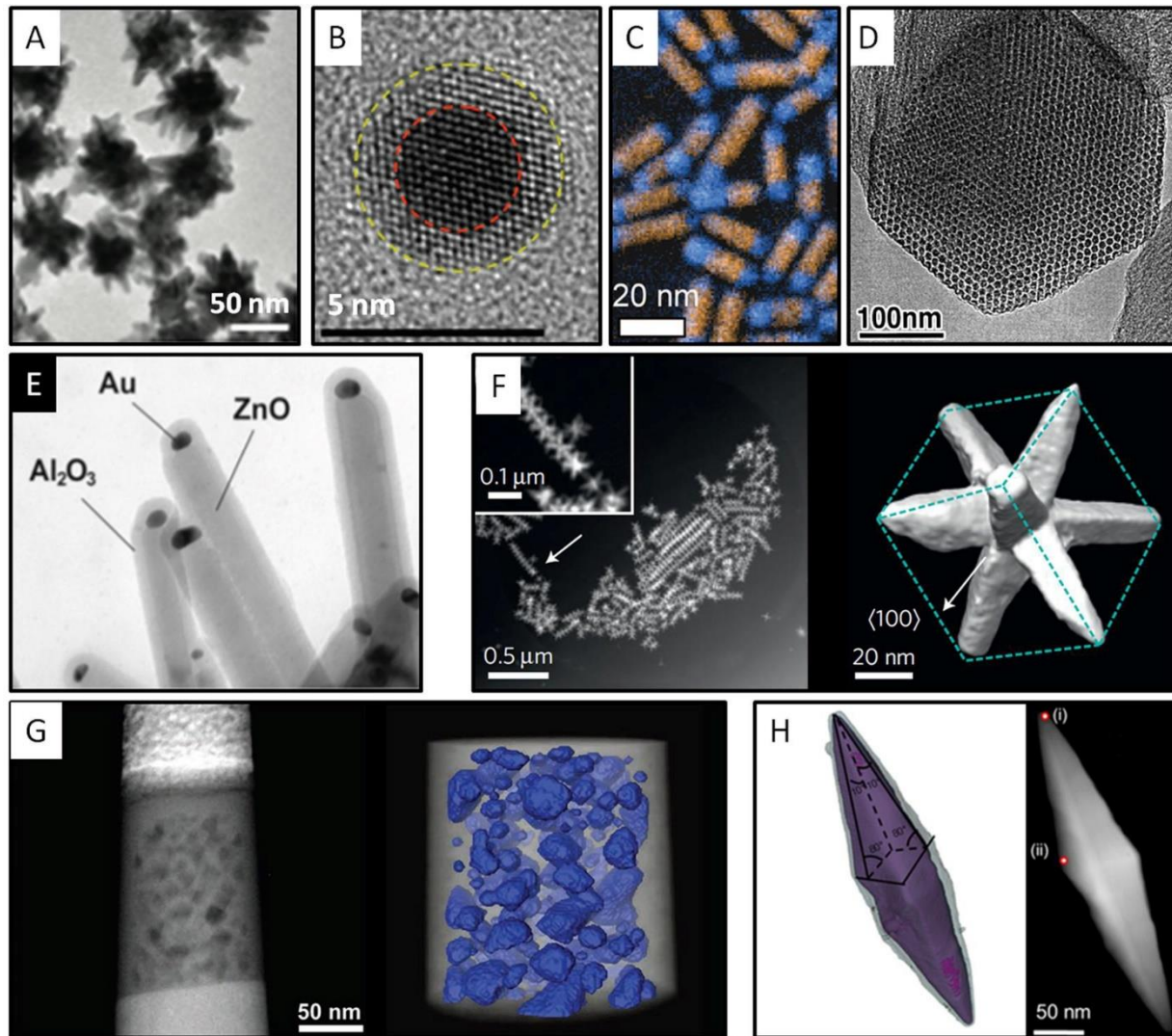
P.H. JOUNEAU (CEA-Minatec), T. EPICIER (MATEIS), unpublished

1-2 nm Au NPs on SBA15

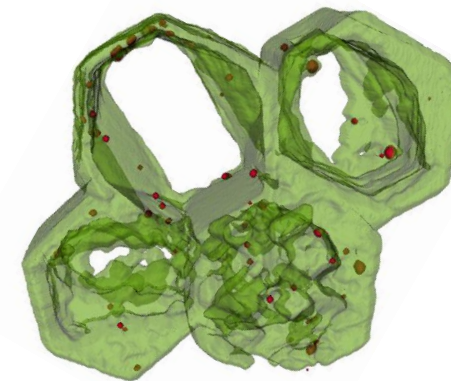
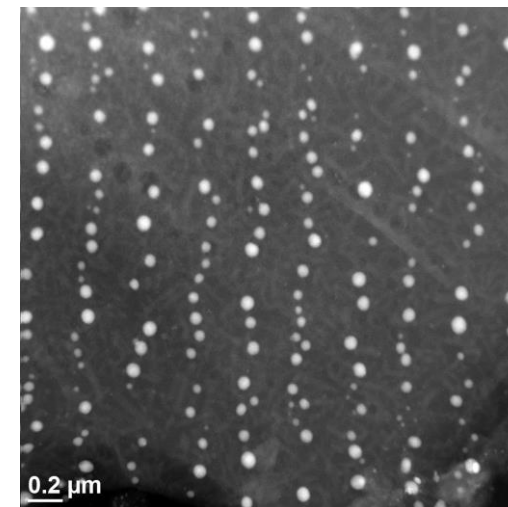


A. MALCHERE, T. EPICIER (MATEIS), unpublished

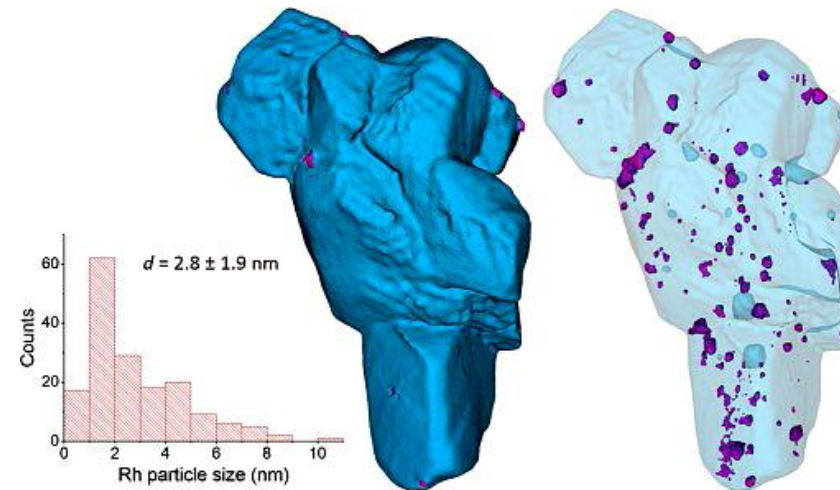
A great variety of 2D/3D NPs arrangements



N. DESTOUCHES et al., *J. Mat. Chem. C* **2** 31 (2014) 6256



L. ROIBAN et al., *J. of Microscopy*, **269** (2018) 117-126

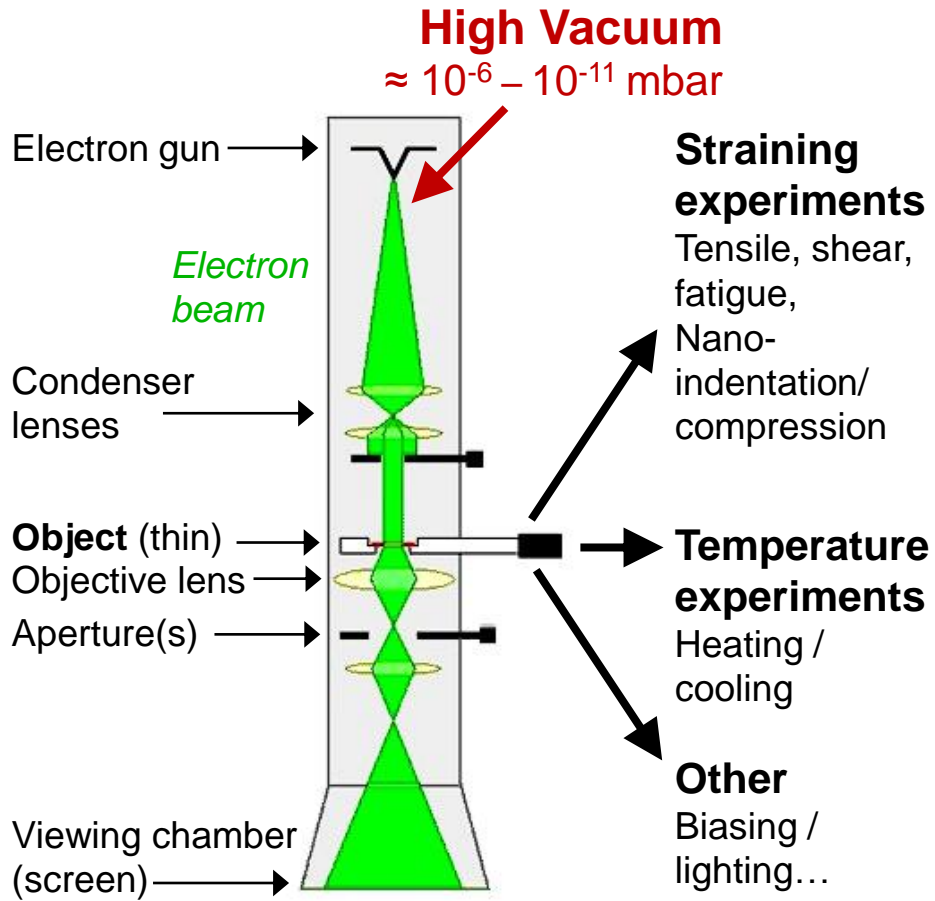


L. ROIBAN et al., *ChemCatChem* **9** (2017) 4607-4613

S. CARENCO et al., *Nanoscale* **8** (2016) 1260-1279

Beyond High Vacuum: Environmental TEM...

• Environmental EM: a technical issue

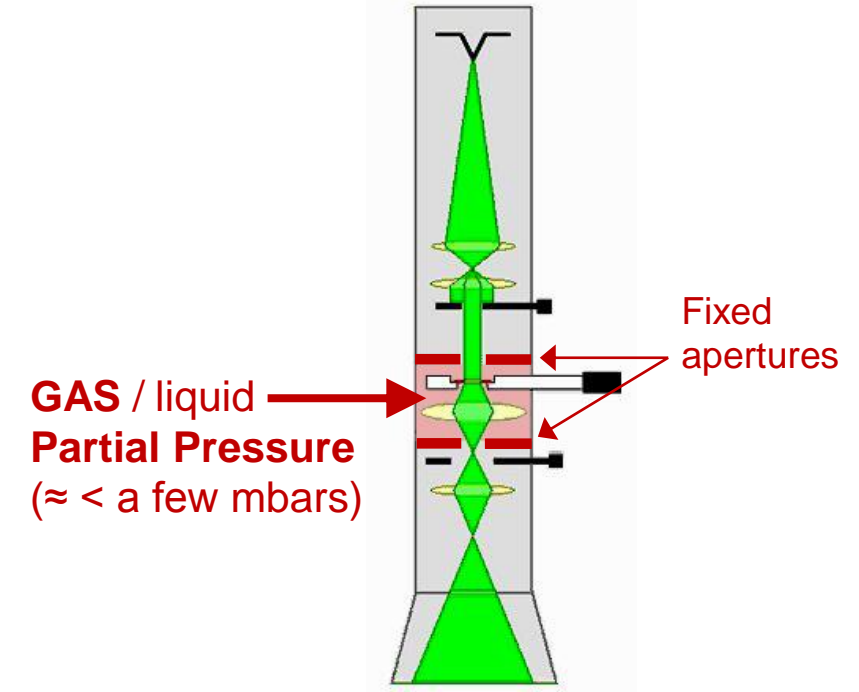


Ladislaus Lazlo MARTON

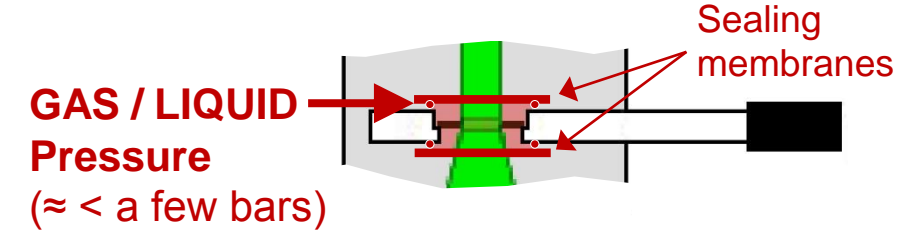
- (a) a pair of electron transparent 'windows' can be placed above and below the specimen to seal it, and its gas atmosphere, from the column;
- (b) alternatively a pair of small apertures can be placed above and below the specimen. Gas leakage into the column is then limited to that which escapes via the apertures.

L. MARTON *Bull. Acad. Roy. Belg. Cl. Sci.* **21** (1935) 553-564

1. Dedicated ETEM (Environmental TEM)

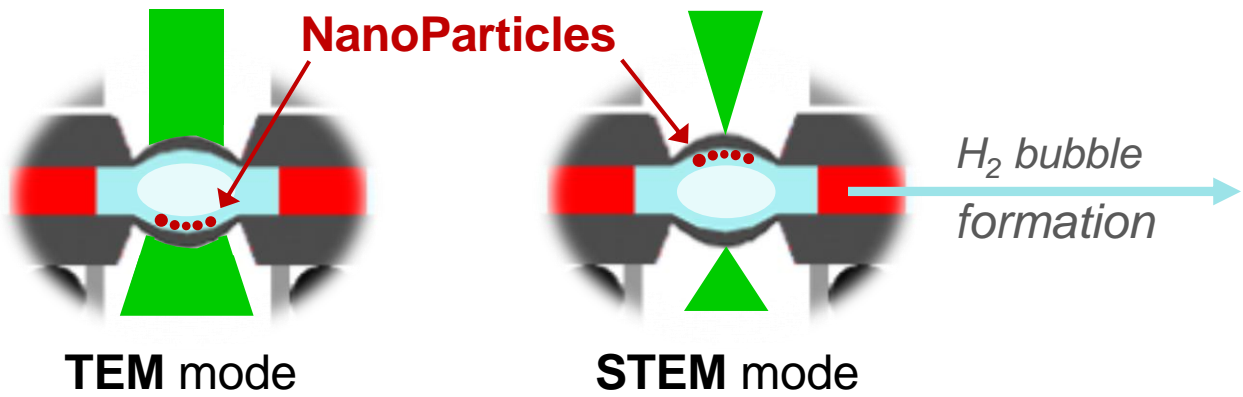
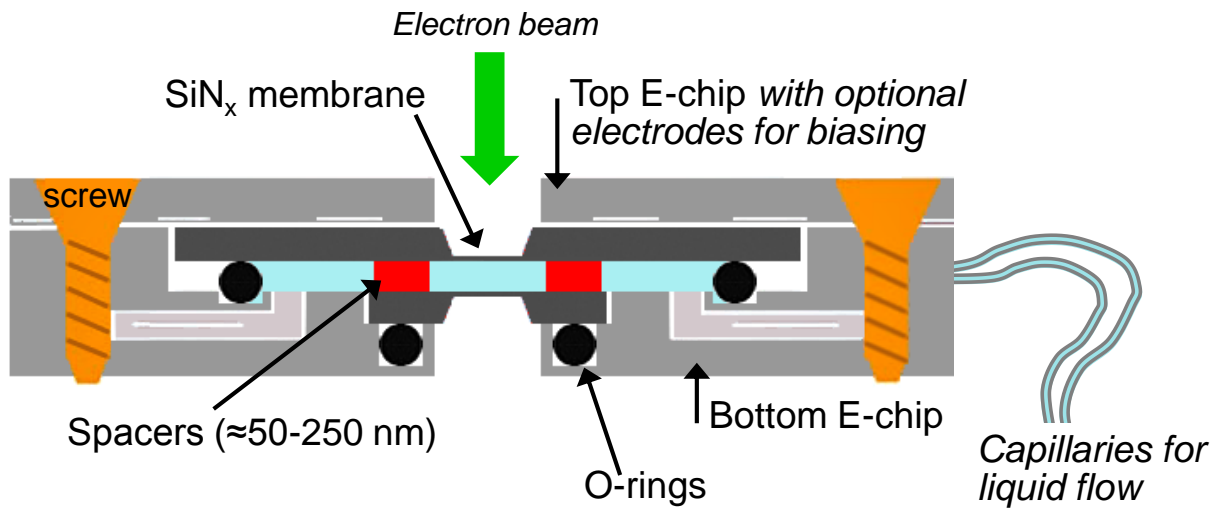


2. Ecell (Environmental closed Cell)



Liquid TEM in E-CELL at P_{atm} : playing with radiolysis

Typical commercial liquid E-Cell



• Some references...

N. de JONGE, F. ROSS, *Nature Nanotech.* **6** (2011) 695
 L. LUTZ et al., *Nano Lett.* **18** (2018) 1280-1289
 N. de JONGE et al., *MRS Bulletin* **41** (2016) 791-799
 'Liquid Cell Electron Microscopy', ed. F.M. ROSS, Cambridge Univ. Press, (2016)
 N. de JONGE, D.B. PECKYS, *ACS Nano* **10** (2016) 9061-9063
 L.R. PARENT et al., *Acc. Chem. Res.* **51** 1 (2018) 3-11

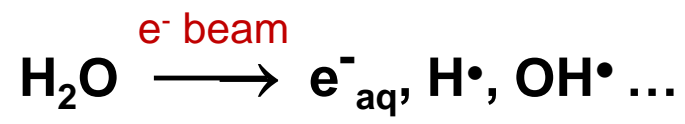
• Commercial providers:


protochips.com


denssolutions.com


hummingbirdscientific.com

Radiolysis of water:



hydrated electrons (e_h^-),
 hydrogen radicals ($\text{H}\cdot$),
 hydroxyl radicals ($\text{OH}\cdot$),
 dihydrogen (H_2),
 hydrogen peroxide (H_2O_2),
 hydronium ions (H_3O^+),
 hydroperoxyl radicals ($\text{HO}_2\cdot$)

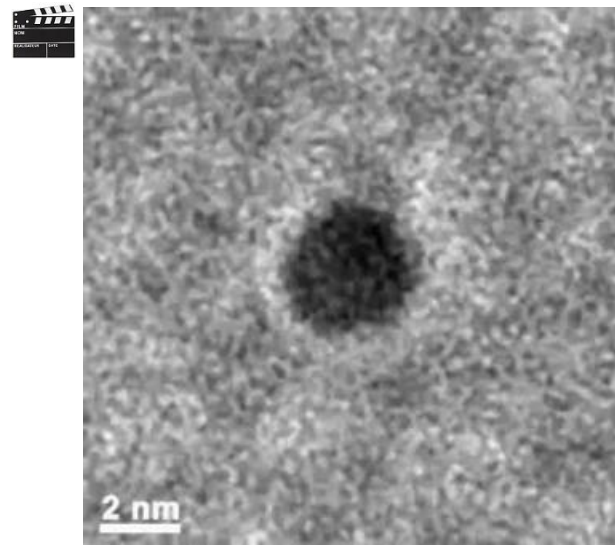
J.M. GROGAN et al., *Nanoletters* **14** (2014) 359-364

Liquid TEM in E-CELL at P_{atm} : playing with radiolysis

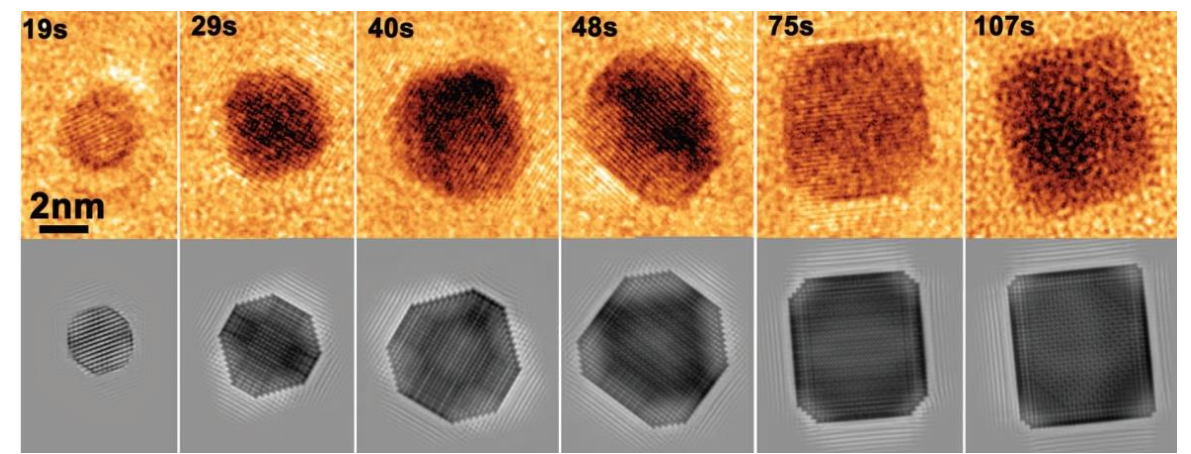
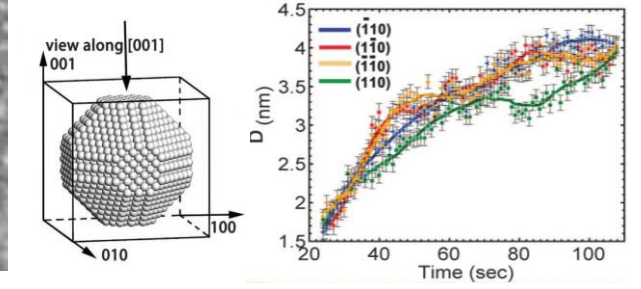
Growth of Pt NPs in liquid

Pt (acetylacetonate)₂ solution (solvent oleylamine / oleic acid / Pentadecane)

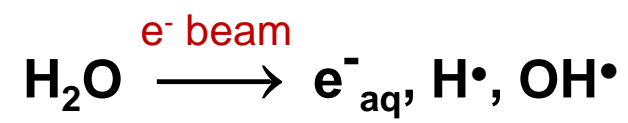
Hong-G. LIAO et al., *Science* **345** (2014) 916



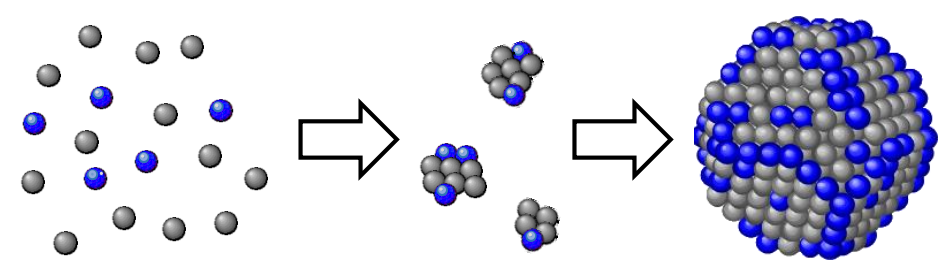
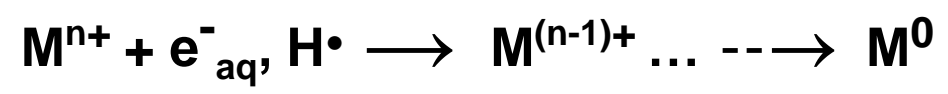
www.sciencemag.org/content/suppl/2014/08/20/345.6199.916.DC1.html



Radiolysis of water:



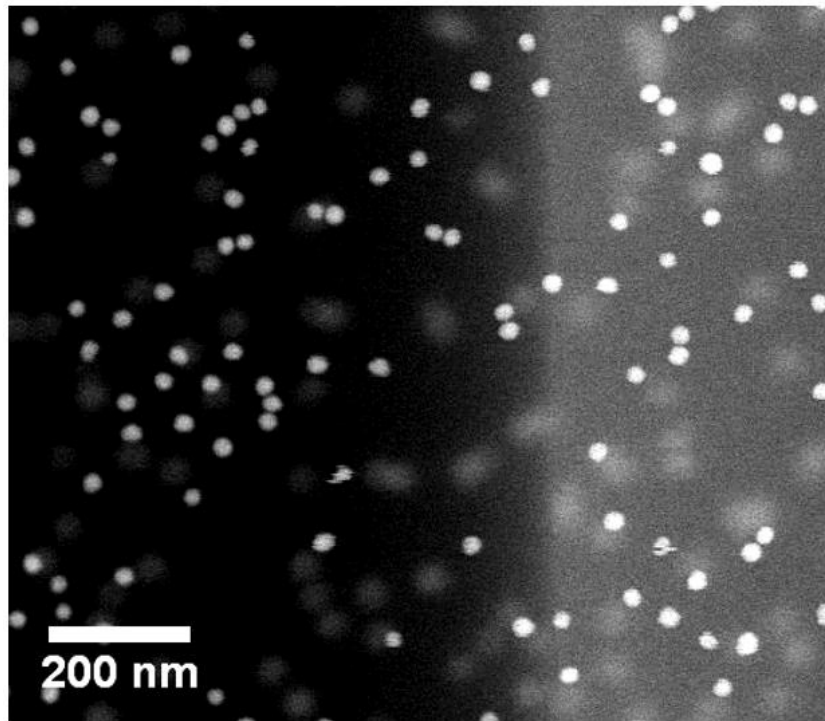
reduction of metal precursor cations:



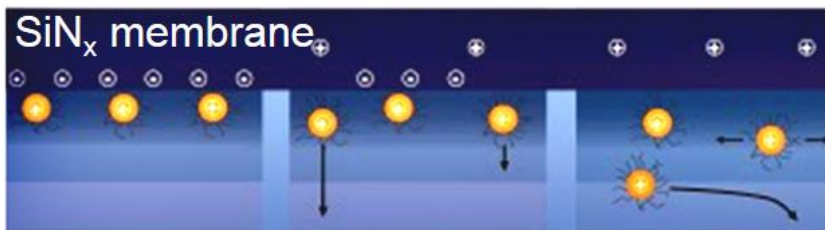
Liquid TEM in E-CELL at P_{atm} : illustrations

- **TCHIT coated gold nanoparticles**

A. VERCH et al., *Langmuir* 31 (2015) 6956-6964

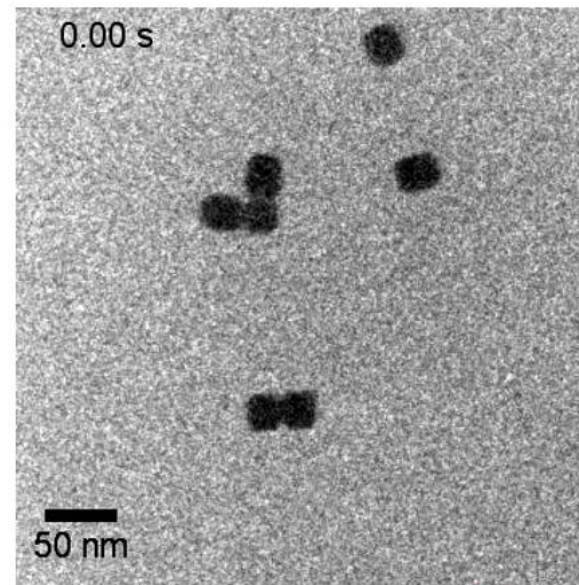


pubs.acs.org/doi/suppl/10.1021/acs.langmuir.5b00150



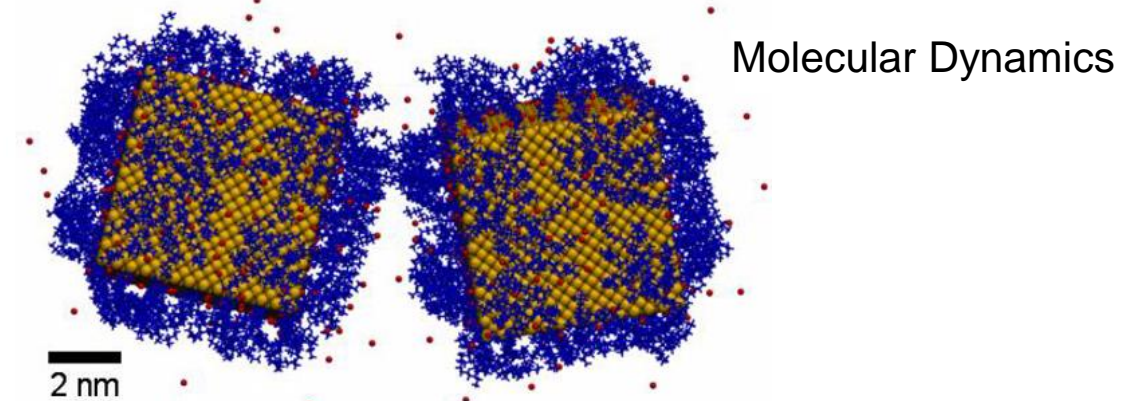
- **CTA⁺-capped gold nanocubes in an aqueous solution**

Br⁻ counterions, cationic surfactants (CTA⁺)



Shu Fen Tan et al., *Adv. Mater* (2018) 1707077

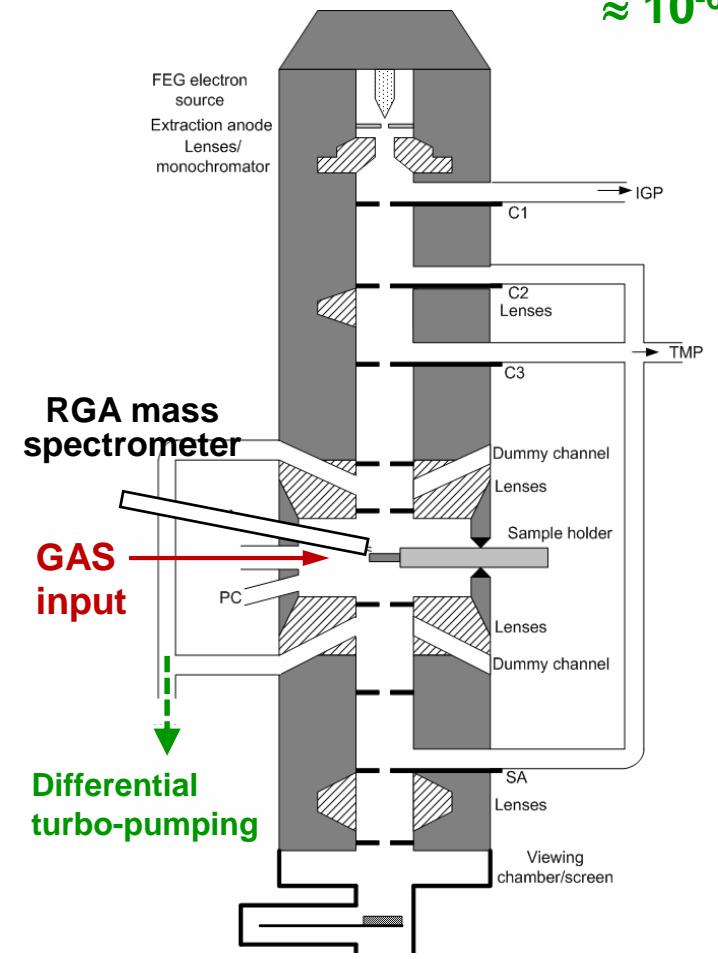
onlinelibrary.wiley.com/doi/abs/10.1002/adma.201707077



Molecular Dynamics

Beyond High Vacuum: Environmental TEM...

Aberration-corrected **FEI TITAN ETEM, 80-300 kV**
 at Univ. Lyon, F



Controlled pressure range:
 $\approx 10^{-6}$ mbar – a few mbar



Equipped with:

- EDX SDD analyzer
- Gatan Imaging Filter
- Tomographic holder
- Heating holders
- Pico-indenter
- Fast 16 Mp CMOS camera Oneview™



25 fps in 4K
 100 fps in 2K

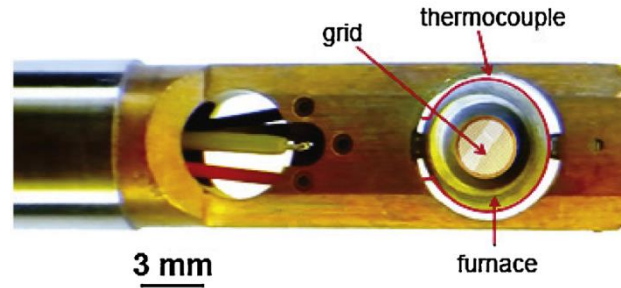
http://www.clym.fr/Ly-EtTEM_examples/Ly-EtTEM_examples.html

Beyond High Vacuum: Environmental TEM...

• Heating specimen holders

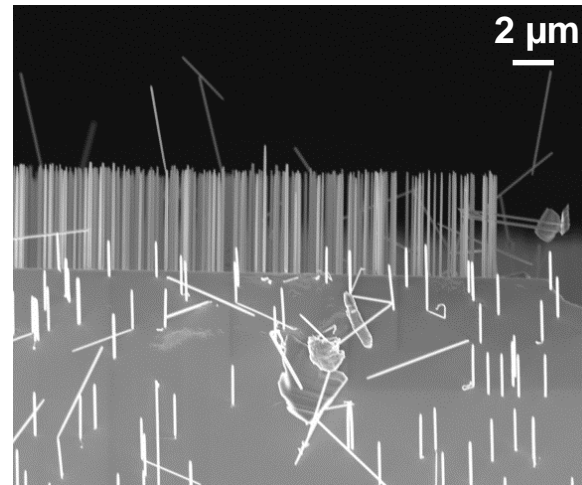
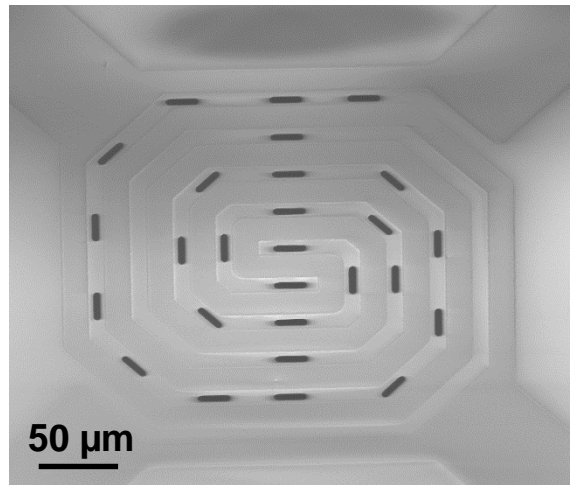
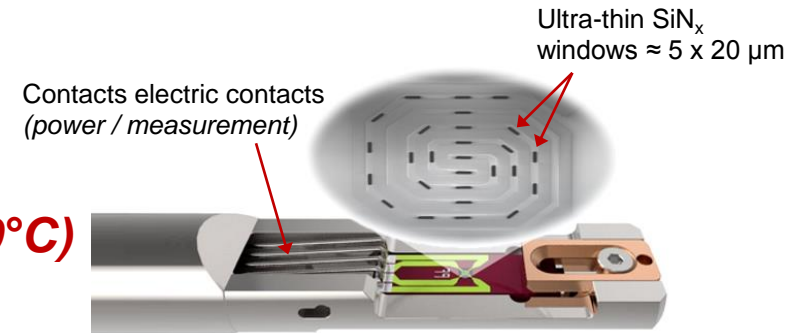
Furnace based (900°C)

www.Gatan.com  GATAN

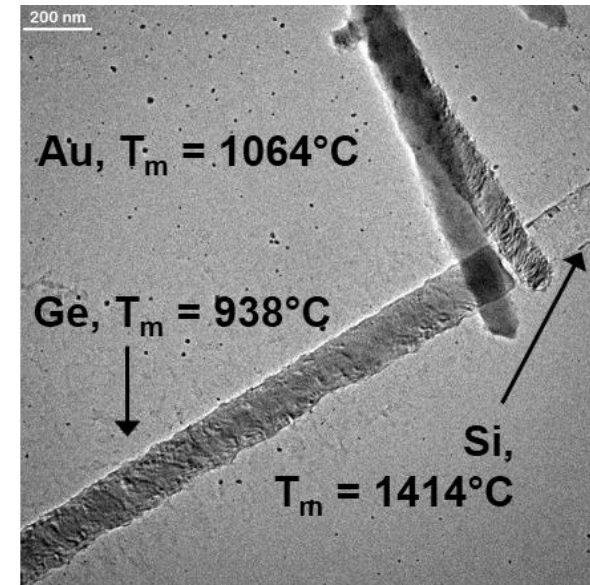


MEMS-based (SiN_x chip) (1300°C)

www.denssolutions.com  DENS solutions



Si@Ge Nanowires
 (M.I. Richard, *Im2np* METSA)



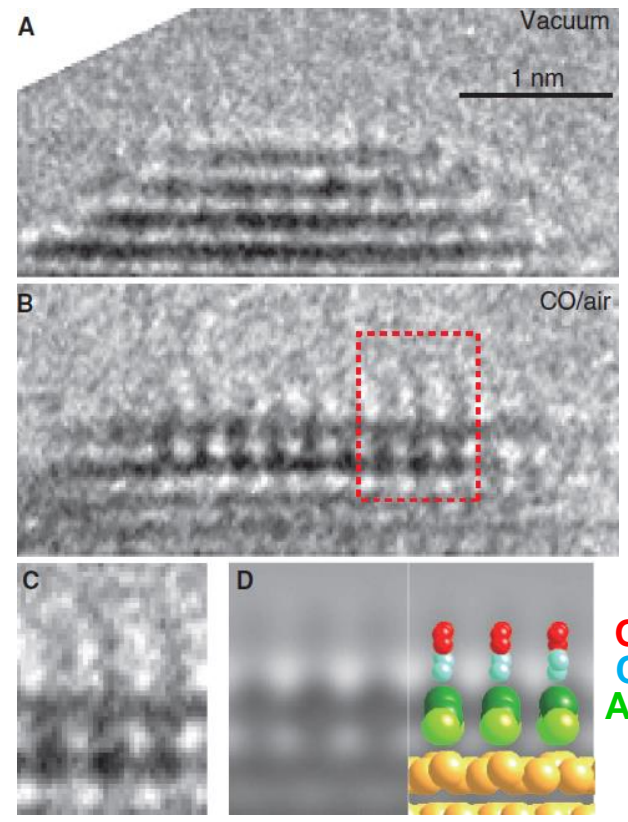
Heating 1100°C (HV)

Speedx10

Atomic imaging at reactive surfaces exposed to gases

Molecule adsorption

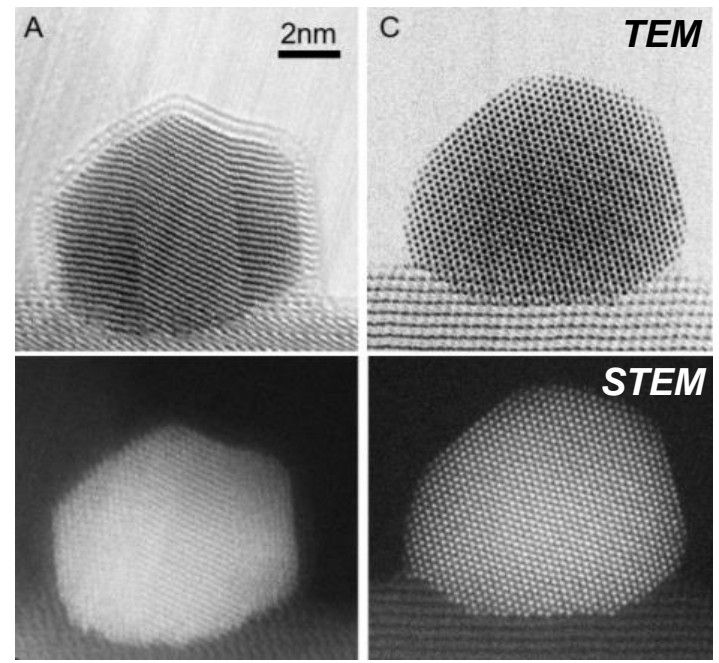
CO on Au (100) (ETEM, 80 kV)
 1% vol. CO in air 1 mbar at 20°C



H. YOSHIDA et al., *Science* **317** (2012) 317-319

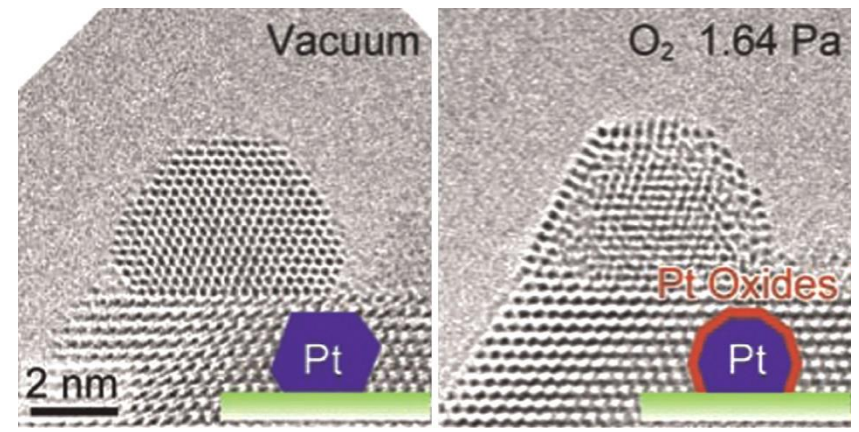
Strong Metal Support Interaction Pd on TiO₂ (TiO_x double layer) (gas E-cell)

H₂ (5 vol %)/Ar, 1 atm at 500°C



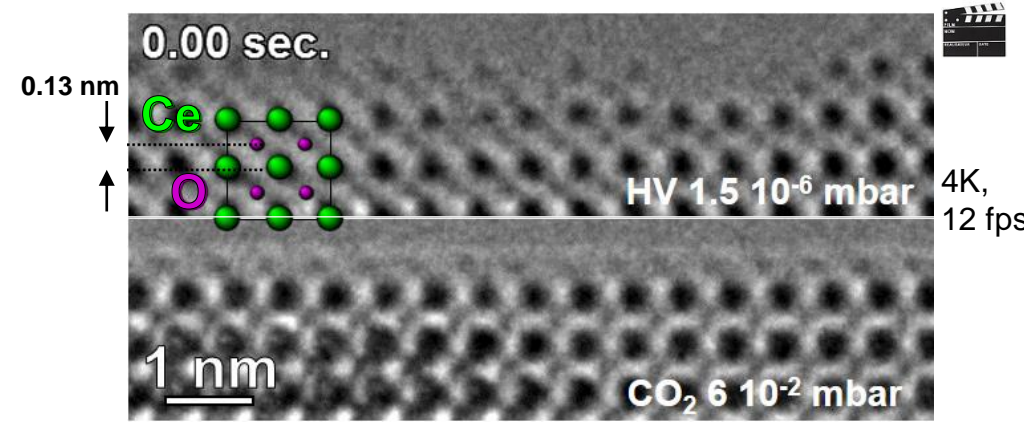
S. ZHANG et al., *Nano-Lett.* **16** (2016) 4528-4534

Partial oxidation Pt on CeO₂ (ETEM) High Vac. vs. O₂ 1.64 10⁻² mbar at 20°C



S. TAKEDA et al., *Ultramicrosc.* **151** (2015) 178-190

Carbonates on CeO₂ {100} surfaces (ETEM) High Vac. vs. CO₂ at 20°C



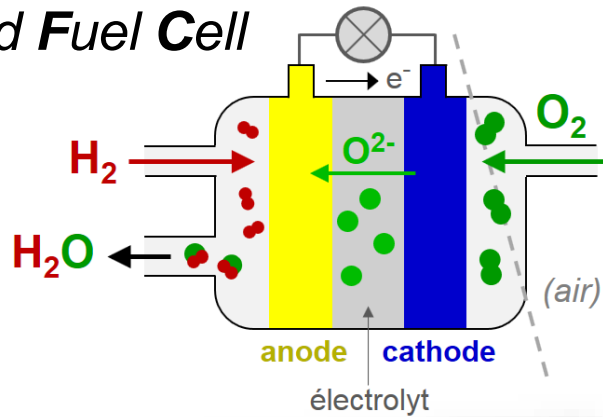
M. BUGNET et al., *Nano Letters* **17** (2017) 7652-7658

SOFC: methane steam reforming for H₂ production

- Context: H₂ production



Solid Fuel Cell



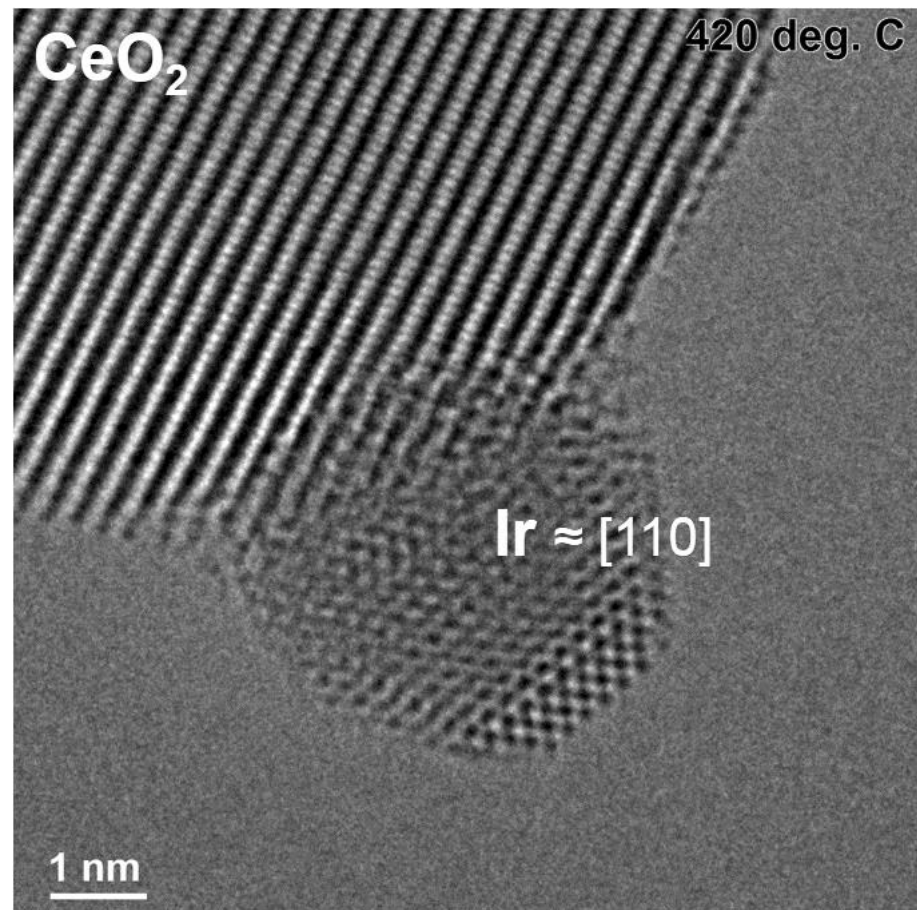
NissanNews.com (2016)

➡ **Catalyst Ir (1%) - CeO₂**

J. TOYIR et al., *Catalysis Today* **157** (2010) 451-455

- Oxydation at low temperature 415 - 480°C (de-activation)

1.2 mbar CH₄-H₂O (≈ 15:1)



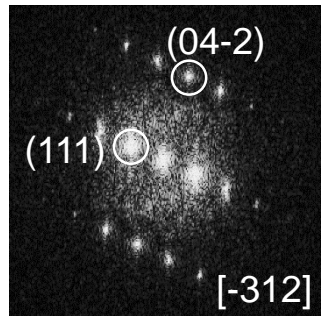
duration ≈ 10 min.

SOFC: methane steam reforming for H₂ production

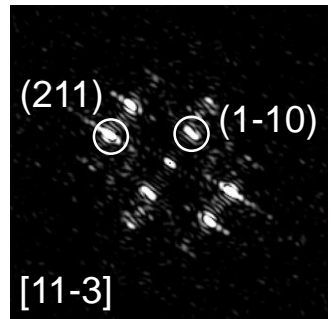
- Oxydation at low temperature 415 - 480°C (de-activation)



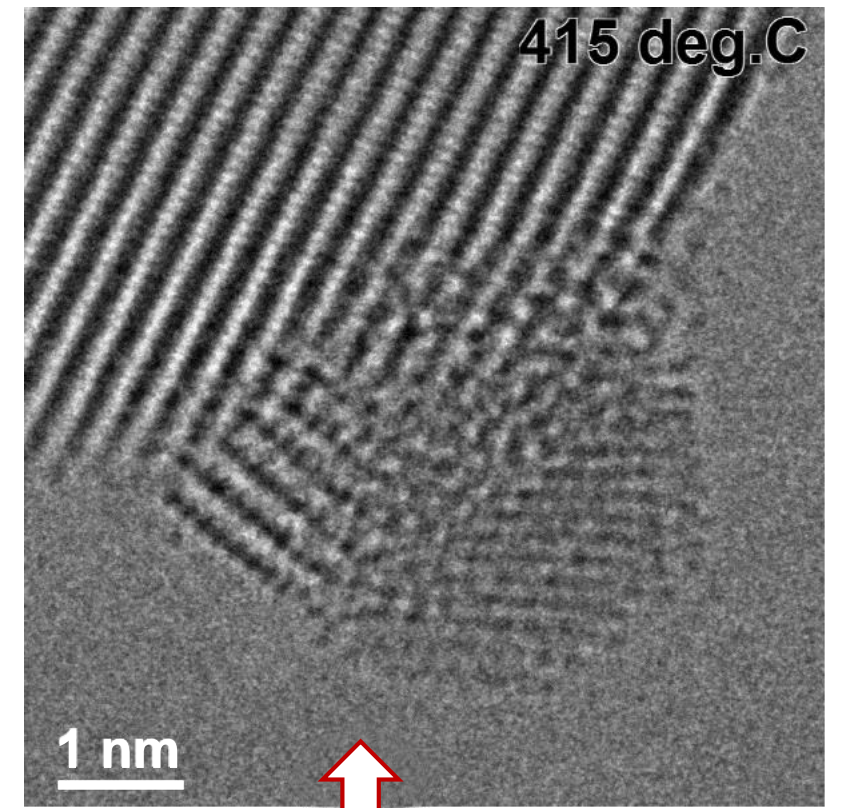
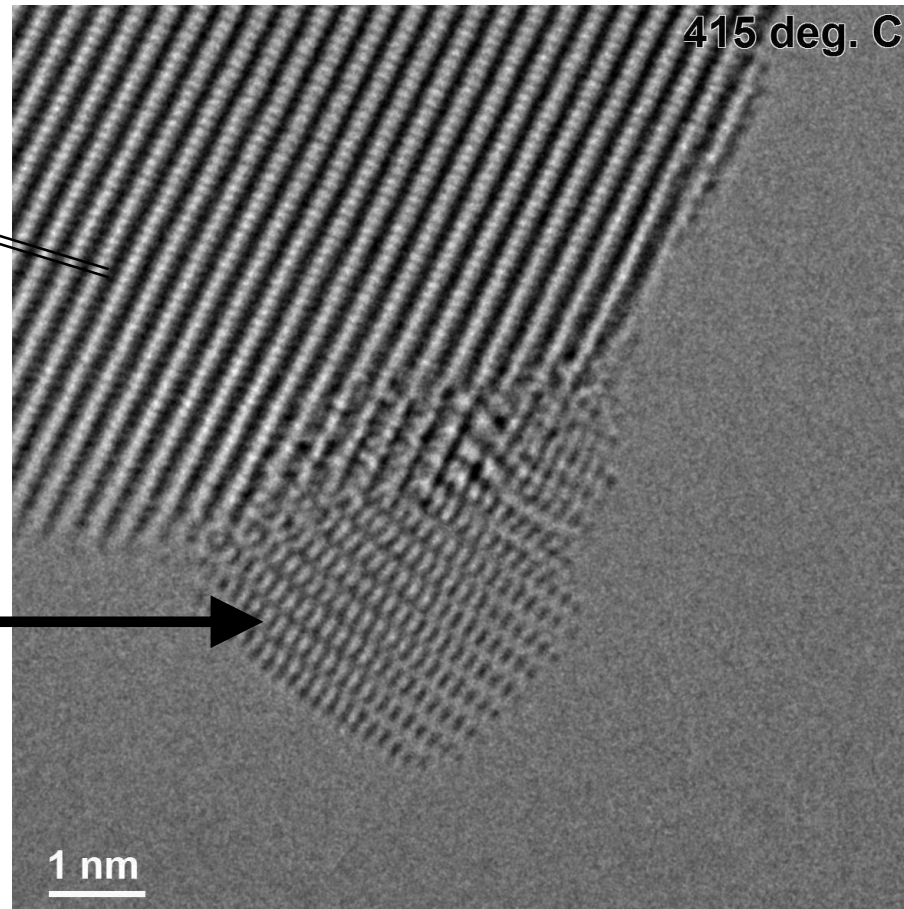
1.2 mbar CH₄-H₂O (≈ 15:1)



CeO₂
0.122 nm

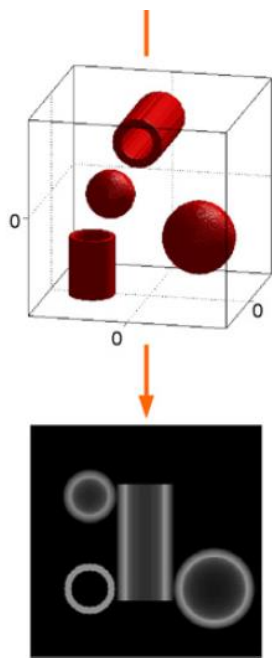


IrO₂
P42/mnm
a=b=0.450 nm
c= 0.315 nm

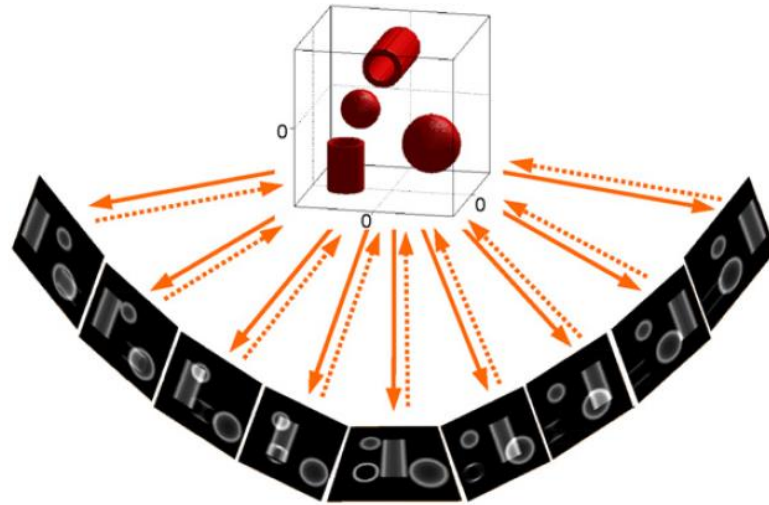


13 fps, average over 2 frames, speed x2

• Conventional tilt tomography in (Transmission) Electron Microscopy



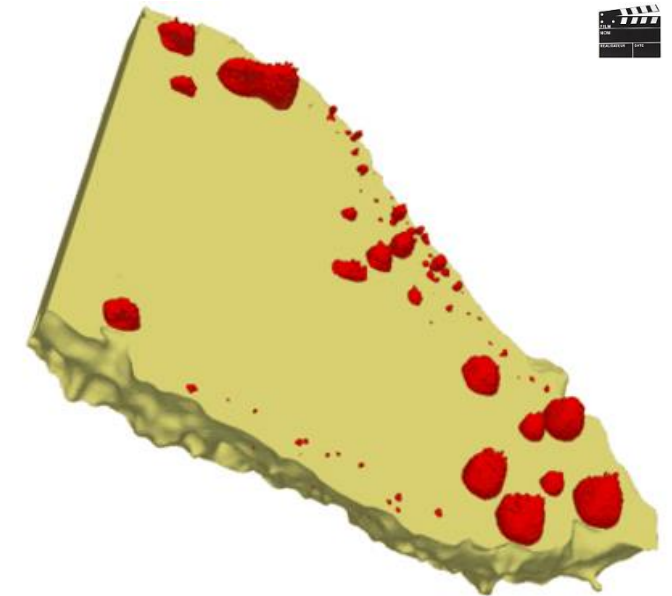
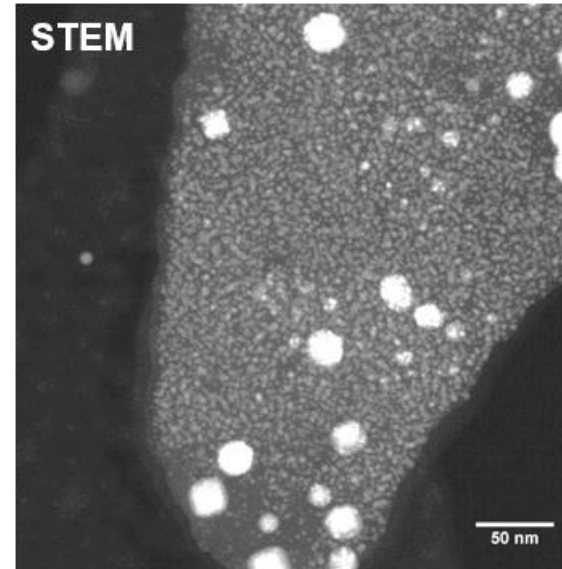
M. BARCENA, A.J. KOSTER, *Seminars in Cell & Developmental Biology*, **20** (2009) 920-930



TILT series of projections at different angles and algorithmic reconstruction

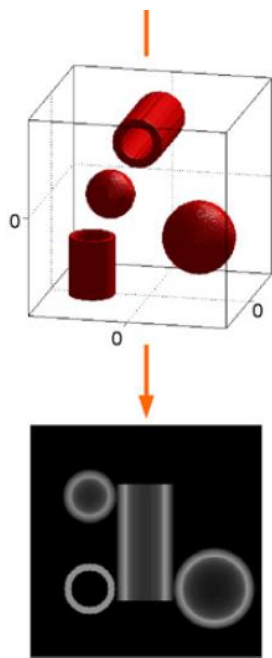
T. EPICIER, p.83-124 in 'Imagerie 3D en Mécanique des Matériaux', Pub. traité MIM, Hermès Sci. (2014)

Plasmonic Au@TiO₂ thin films prepared by reactive DC magnetron sputtering

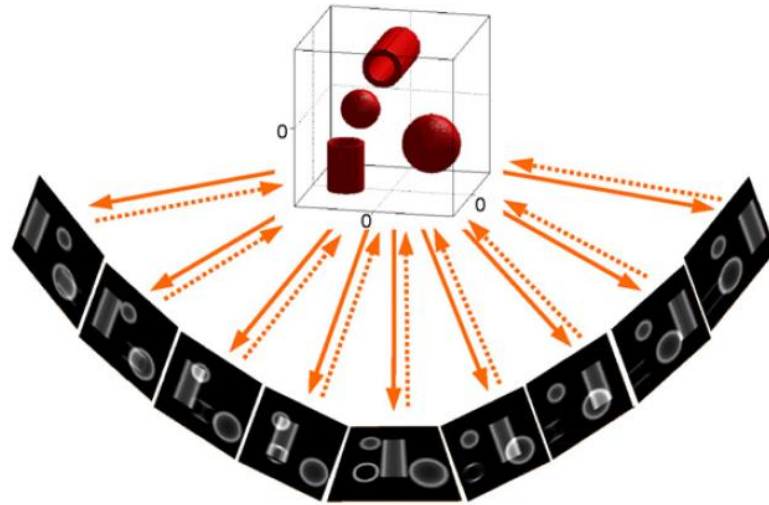


S. KONETI, J. BORGES, L. ROIBAN, M. S. RODRIGUES, N. MARTIN, T. EPICIER, F. VAZ, P. STEYER, *in progress*

- Conventional tilt tomography *is not compatible* with in situ experiments



M. BARCENA, A.J. KOSTER, *Seminars in Cell & Developmental Biology*, **20** (2009) 920-930

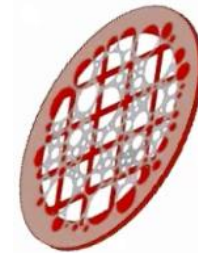


TILT series of projections at different angles and algorithmic reconstruction

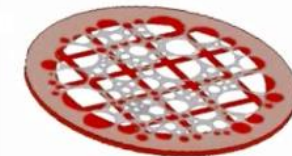
T. EPICIER, p.83-124 in 'Imagerie 3D en Mécanique des Matériaux', Pub. traité MIM, Hermès Sci. (2014)

Classical STEP-BY-STEP 'tilt' tomography

> several minutes in BF (hour in STEM)



'tilt' tomography by CONTINUOUS ROTATION (fast acquisition camera ≈ 100 fps)
 Down to a few seconds in Bright Field



L. ROIBAN et al., *J. of Microscopy*, **269** (2018) 117-126

H. BANJAK et al., *Ultramicroscopy*, **189** (2018) 109-123

• 3D Operando study of the resistance to sintering of Pd@SiO₂ nanocatalysts

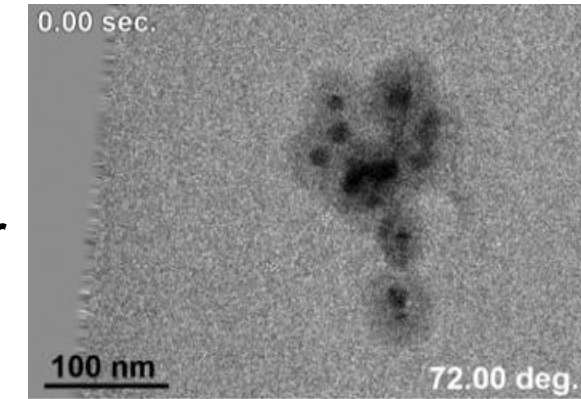
- Tomo acquisitions: **6 to 9 sec (tilting series +72/-71°)**
- 4 mbar H₂, 20 to 500°C,
- e⁻ flux 9.3 10³ e⁻/s.nm², total electron dose **1.4 10⁶ e⁻/nm²**
- Preliminary irradiation test: no visible damage up to **3.9 10⁶ e⁻/nm²**

20°C, 6 10⁻⁷ mbar (HV)

After 35' at 400°C, H₂ 4 mbar

After 60' at 500°C, H₂ 4 mbar

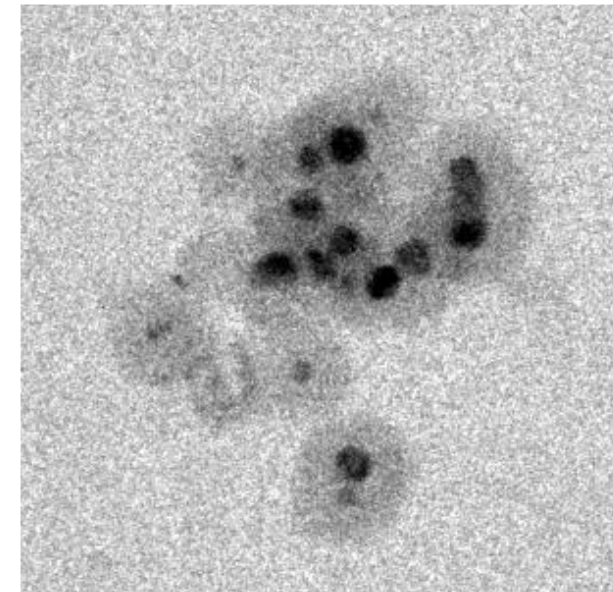
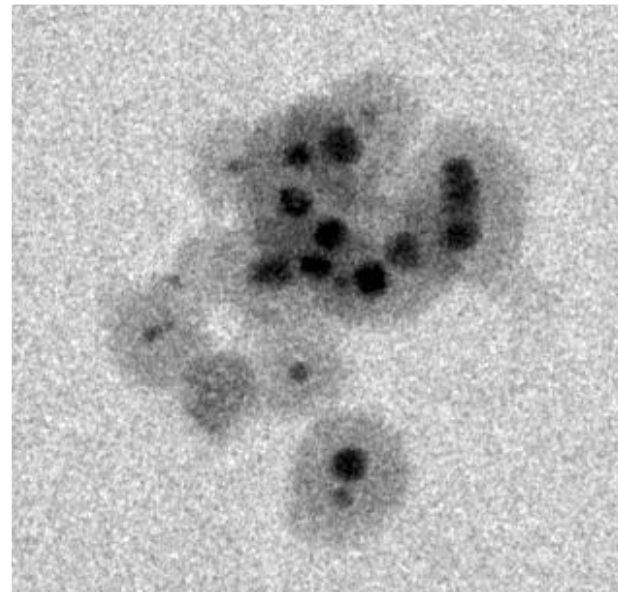
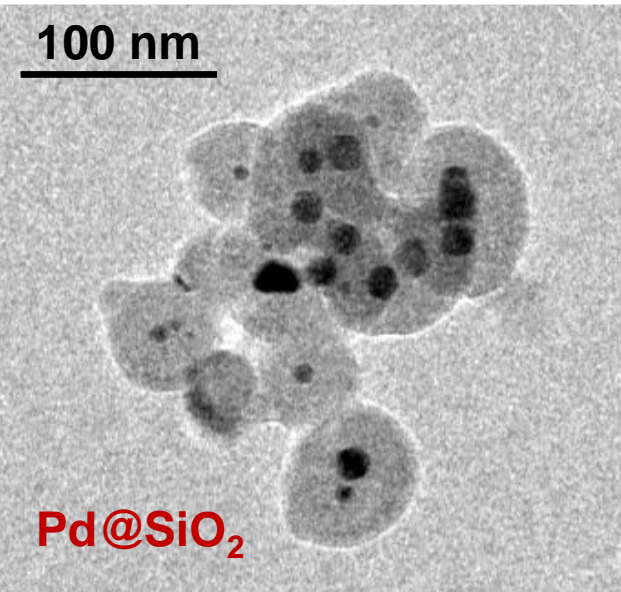
Aligned tilt series



3D model



T. EPICIER et al., *in progress*



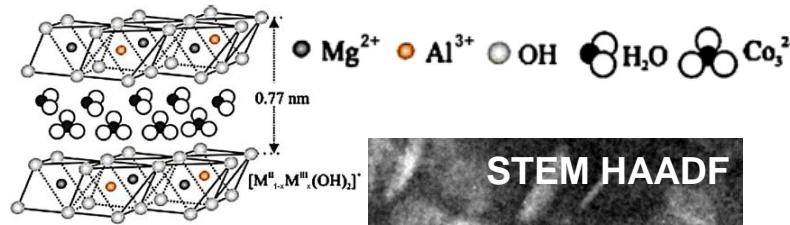
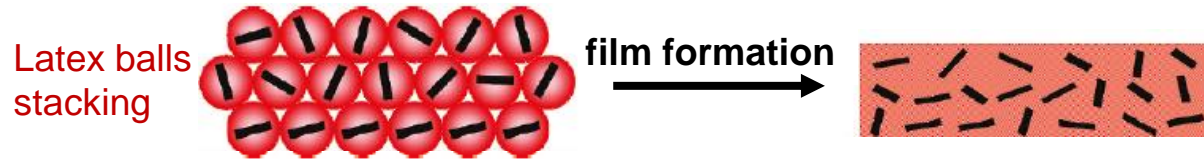
Exposure beam time $t \approx 62$ s,
 cumulative dose = $5.7 \cdot 10^5$ e⁻/nm²

Added exposure beam time $t \approx 87$ s,
 cumulative dose = $1.3 \cdot 10^6$ e⁻/nm²

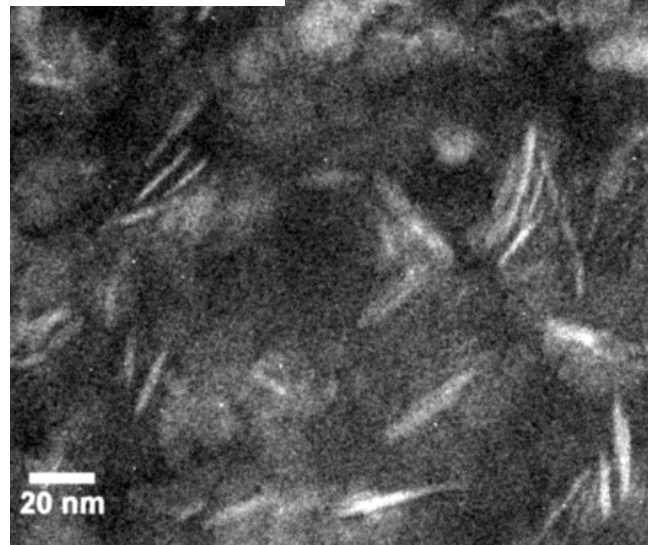
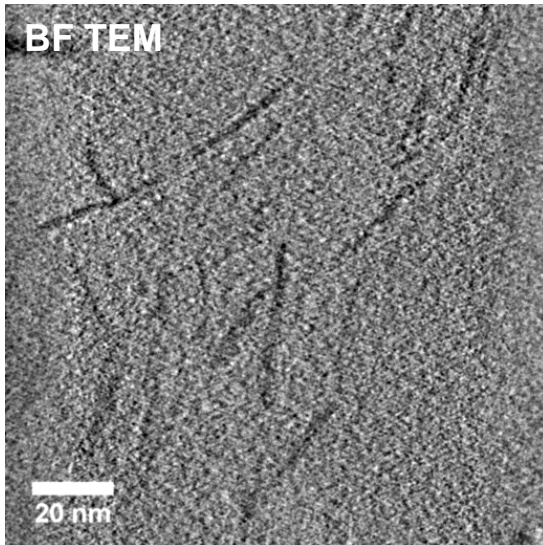
Added exposure beam time $t \approx 18$ s,
 cumulative dose = $1.4 \cdot 10^6$ e⁻/nm²

• Ex.: POLYMER NANOCOMPOSITES (Dispersion of Mg₃AlCO₃ Layer-Double Hydroxide nanoplatelets in latex)

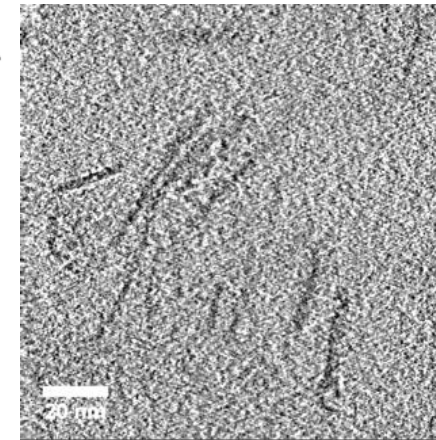
Starch-Based Polymeric Materials and Nanocomposites, ed. J. AHMED, B. K. TIWARI, S. H. IMAM, M.A. RAO, CRC Press, (2012) 416 p.



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



ART Tomogram



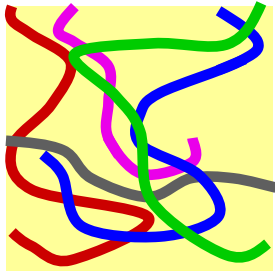
3D model (LDH nanoplatelets)



step-by-step series,
+70 to -70°, 200 sec.
 (pause 0.5 sec,
 total electron dose
 $\approx 2.4 \cdot 10^4 \text{ e}^-/\text{\AA}^2$ *validated*
by an irradiation test)

S. KONETI, L. ROIBAN, F. DALMAS,
 T. EPICIER (*in progress*)

• Ex. SEM: POLYMER NANOCOMPOSITES CNTs@P(S-BuA)



Y. LIU, thèse (2013), INSA-Lyon

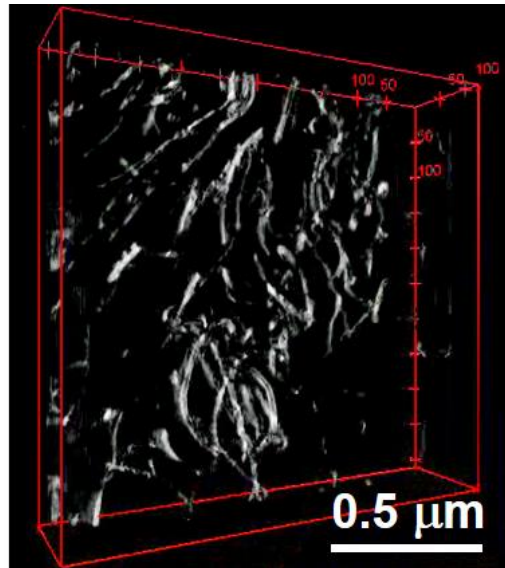
HITACHI S-5500
 Tohoku University
 SENDAI, Japan



• Focused Ion Beam microscope

[L.A. GIANNUZZI et al., p.13-53 in 'Introduction to Focused Ion Beams: Instrumentation, Theory, Techniques and Practice', Springer, New York (2005)]

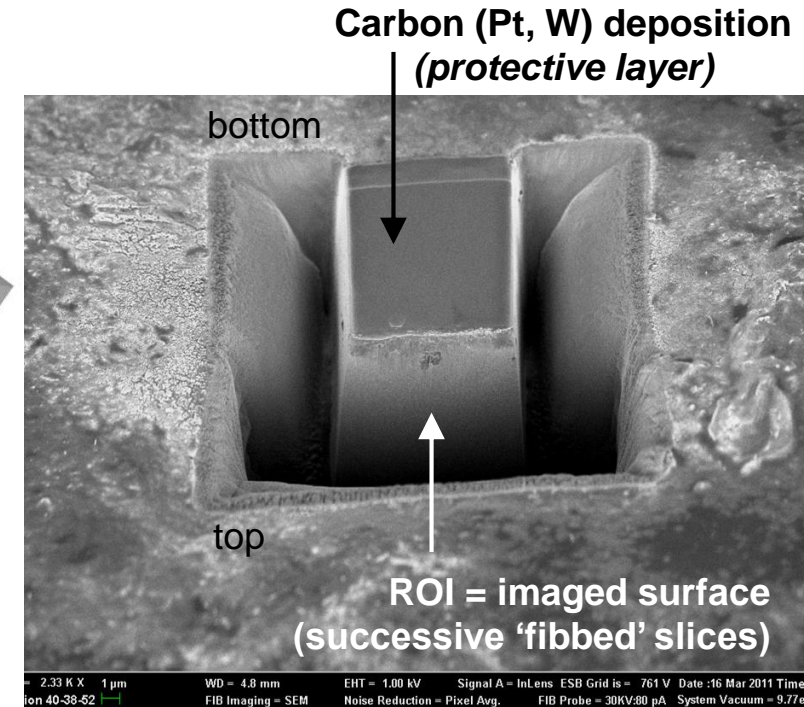
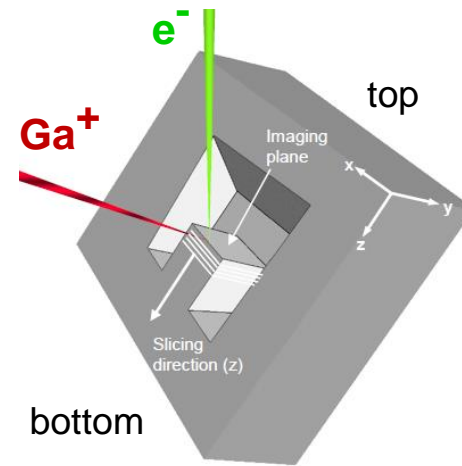
[M. CANTONI, L. HOLZER. *MRS Bulletin*, **394** (2014) 354-360]



'tilt' series, -40° / 40° (step 1°)

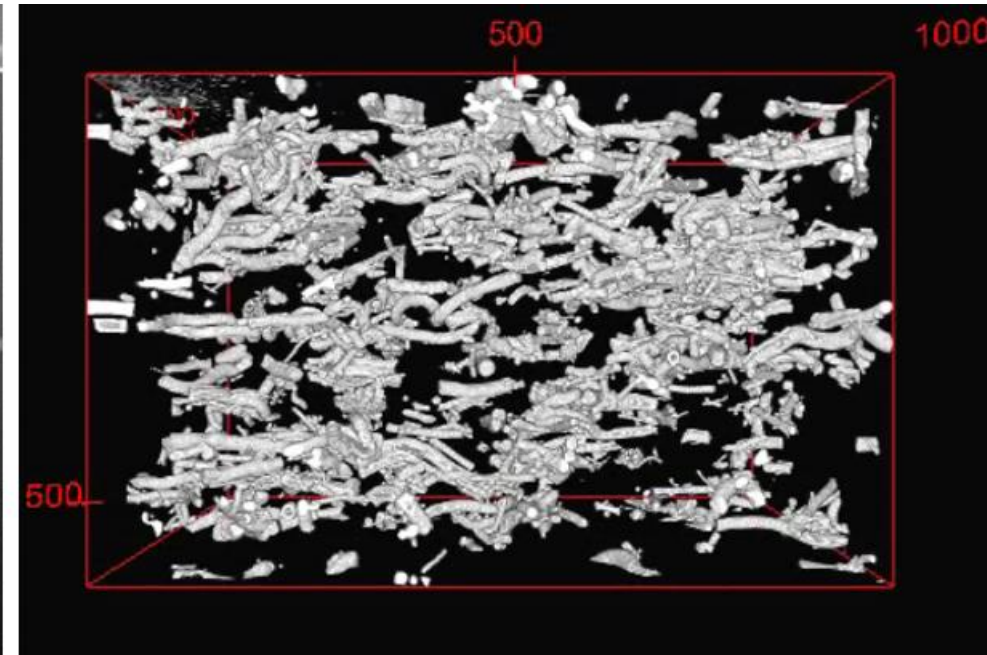
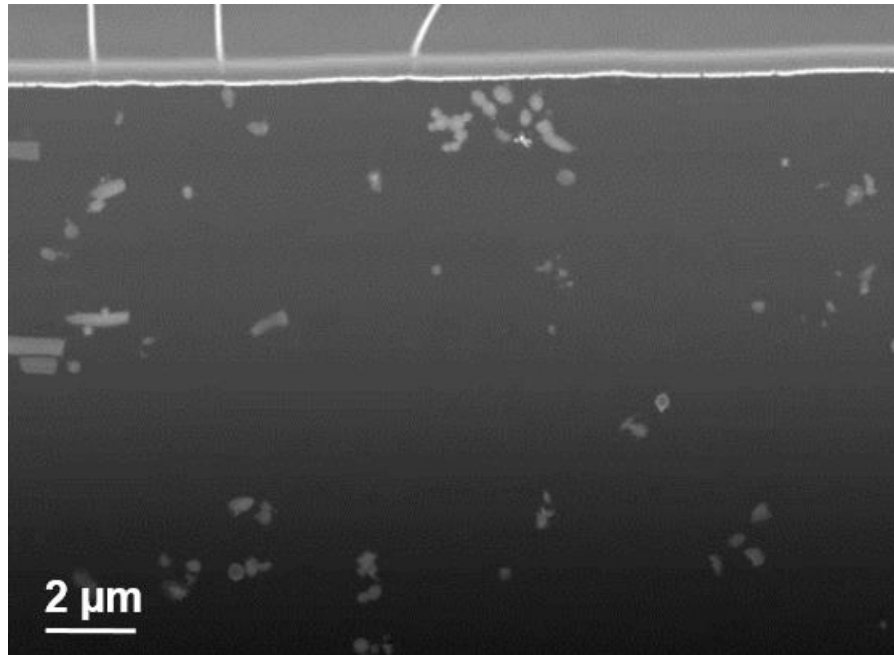
ART 10 iterations
 (thickness ≈ 350 nm)

P. JORNSANOH et al., *Ultramicroscopy* **111** 8 (2011) 1247-1254



- *Ex. FIB*: polyurethane (PU) matrix reinforced with 5 wt.% of Fe₃C@C nanowires

V. SALLES et al., *Sensors and Actuators A*, **211** (2014), 105-114



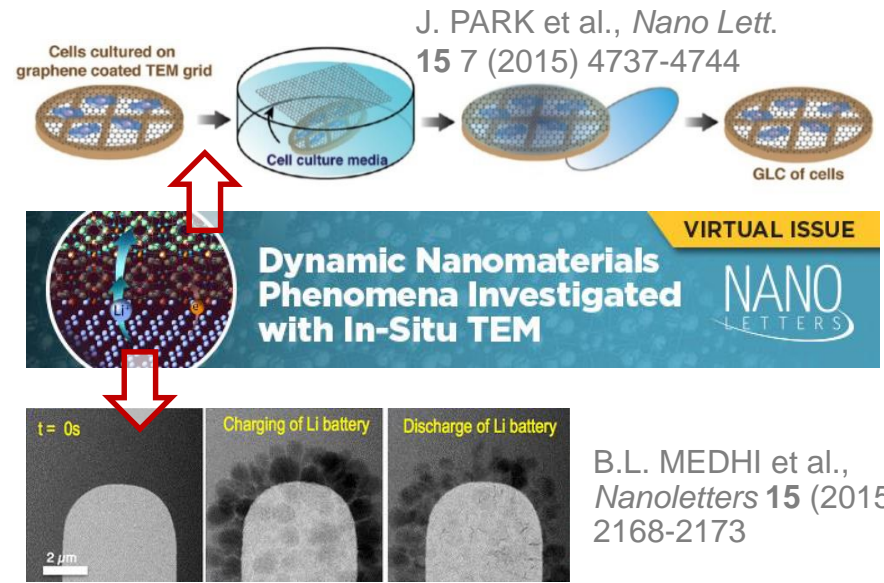
760 slices, thickness 20 nm

- Typical resolution (isotropic voxel): ≈ 3 nm
- Typical volumes in (*more than*) a few hours : $15 \times 10 \times 10 \mu\text{m}^3$
- *Hundreds to Thousands of images*

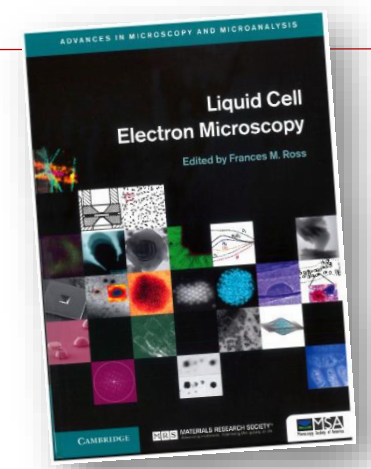
CONCLUSIONS *(further reading...)*

• Important applications of LIQUID (ST)EM

- **Biological matter**
 (tissues / cells, interactions with NPs)
- **Electrochemistry**
 (development of batteries)
- **Liquid microscopy in the Scanning Electron Microscope**



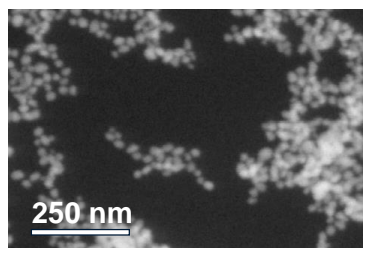
'Liquid Cell Electron Microscopy',
 ed. F.M. ROSS, Cambridge Univ.
 Press, (2016)



M.T. McDOWELI et al.,
Nano Lett. **18** (2018) 657-659

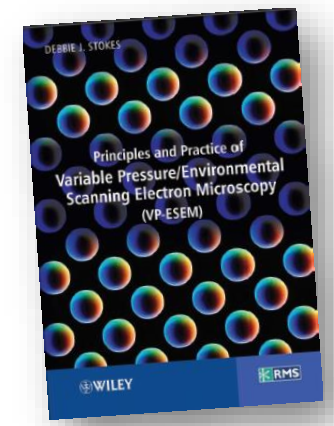
B.L. MEDHI et al.,
Nanoletters **15** (2015)
 2168-2173

A. BOGNER et al., *Micron*
38 (2007) 390-401

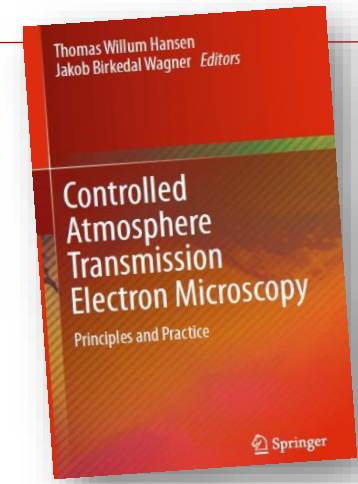


Gold NPs
 (20 nm) in water

'Principles and Practice
 of Variable Pressure /
 Environmental Scanning
 Electron Microscopy (VP-
 ESEM)', ed. D. STOKES,
 Wiley, (2008)



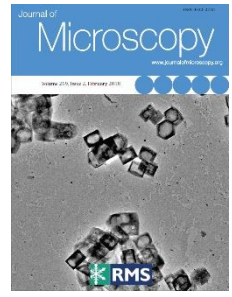
CONCLUSIONS *(further reading...)*



'Controlled-Atmosphere TEM', eds. T.W. HANSEN, J.B. WAGNER, Springer (2016)

- Other developments of (E)TEM on NPs

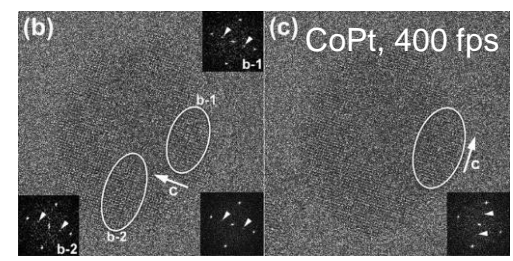
- Specific ETEM experiments



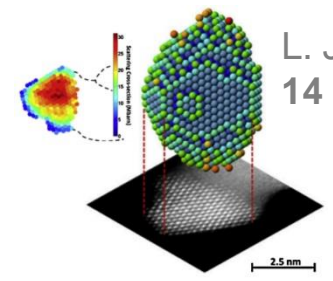
T. EPICIER, M. RAINFORTH, *J. of Microscopy*, **269** 2 (2018) 115-116

- Fast imaging of dynamical processes

K. SATO, H. YASUDA, *APL* **110** (2017) 153101

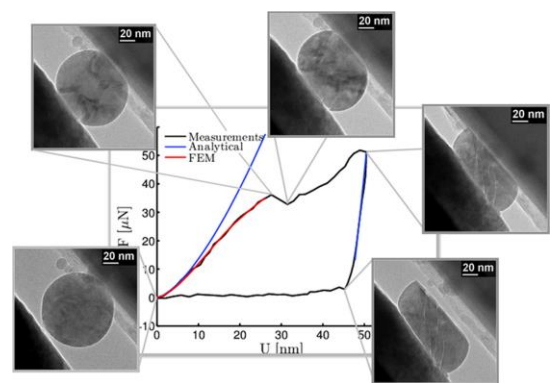


- 3D at atomic resolution



L. JONES et al., *Nano Lett.* **14** (2014) 6336-6341

- In situ mechanical properties (nanocompression)



E. CALVIÉ et al., *Materials Letters* **119** (2014) 107-110