"Tri-3D" Tomography in FIB, SEM and TEM: Application to Polymer Nano-Composites

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1 µm

Available tomography approaches in Materials Science

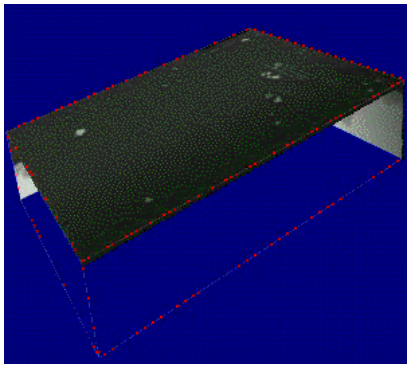
µm ⇨ nm ⇨ Å

X-Ray Tomography

J.Y. BUFFIÈRES *(MATEIS,INSA-Lyon)*, T. CONNOLLEY *(Galway, IRELAND)*

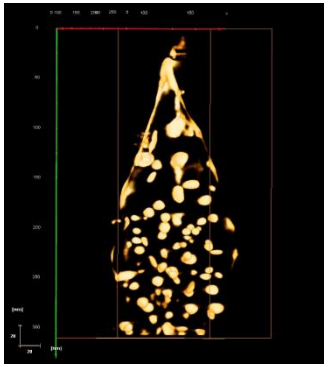
SEM / FIB

A. BOGNER, Y. LIU, T. EPICiER *(INSA-Lyon)*



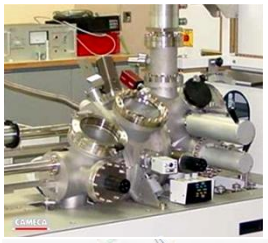
CLYM: B. VAN DE MOORTELE *(ENS-Lyon)*, A. DESCAMPS *(INSA-Lyon)*, N. BLANCHARD *(Lyon 1 University)*, T. DOUILLARD, T. EPICiER *(INSA-Lyon)*

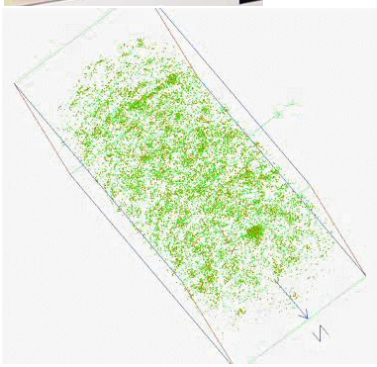
TEM



S. BENLEKBIR, T. EPICIER, *(MATEIS, INSA-Lyon)*, F. DANOIX *(GPM-Rouen)*

Atom Probe Tomography / Field-Ion Microscopy





F. DANOIX *(GPM-Rouen)*, *M. PEREZ, T. EPICIER (MATEIS, INSA-Lyon), F. DE GEUSER, A. DESCHAMPS (SIMAP-Grenoble)*

Available tomography approaches in Materials Science

µm ⇨ **nm** ⇨ **Å**

X-Ray Tomography

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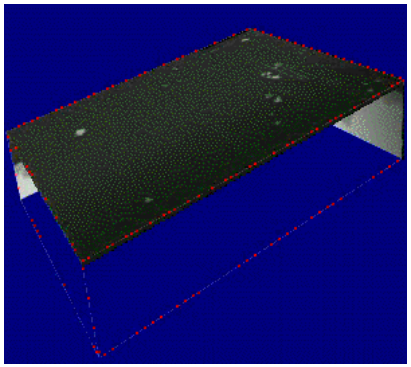
SEM / FIB

A. BOGNER, Y. LIU, T. EPICiER *(INSA-Lyon)*



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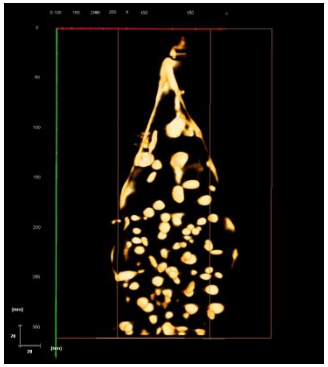
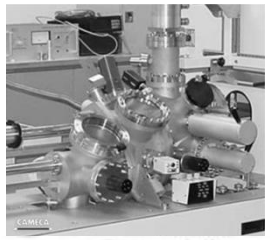
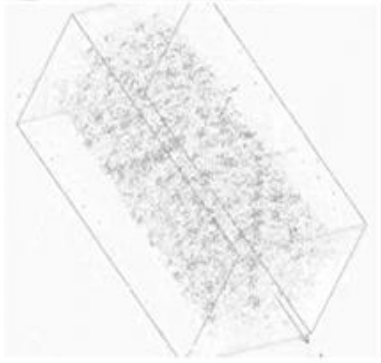
TEM



S. BENLEKBIR, T. EPICIER, *(MATEIS, INSA-Lyon)*, F. DANOIX *(GPM-Rouen)*

Atom Probe Tomography / Field-Ion Microscopy





F. DANOIX *(GPM-Rouen)*, M. PEREZ, T. EPICIER *(MATEIS, INSA-Lyon)*, F. DE GEUSER, A. DESCHAMPS *(SIMAP-Grenoble)*

Multi-scale approach developed at MATEIS

OUTLINE

I. Materials and Techniques

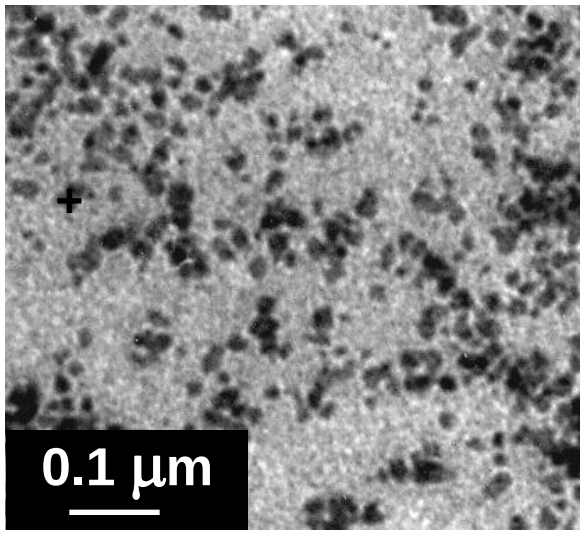
I.1 Polymer-based nano-composites

ancient Maya's paintings

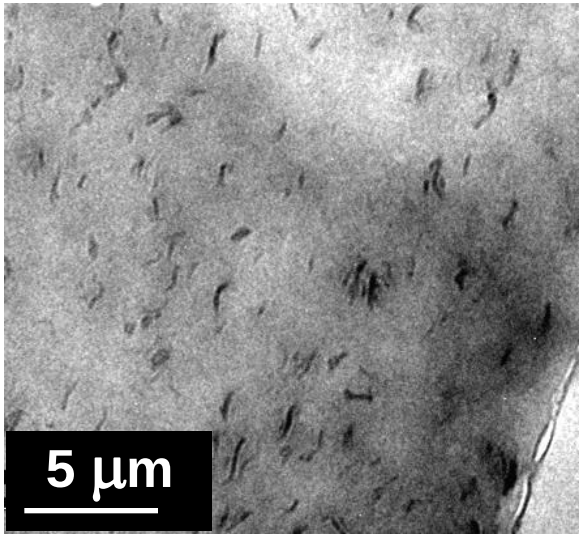
1917

1990's

PHEMA, 5% SiO_2

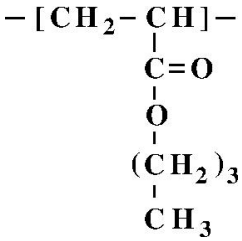


Montmorillonite in polyamide 6
$(Na,Ca)_{0,3}\ (Al,Mg)_2\ Si_4\ O_{10}\ (OH)_2\ nH_2O$

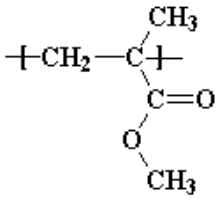


I. Materials and Techniques

I.2 Studied system: PMMA/PSBuA – SiO_2



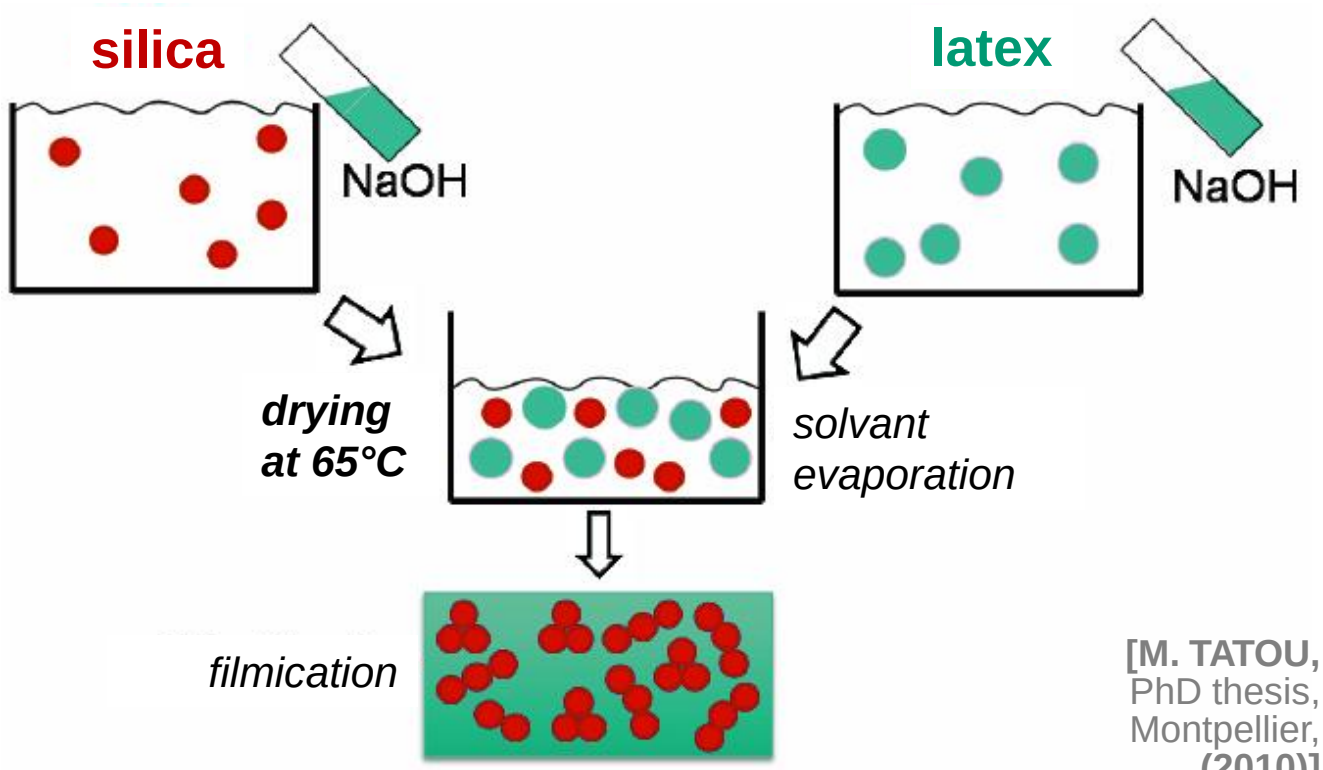
BUA



MMA

+

x (1-5) %
SiO_2, various PH,
mean NP diameter:
16 nm



[M. TATOU, PhD thesis, Montpellier, (2010)]

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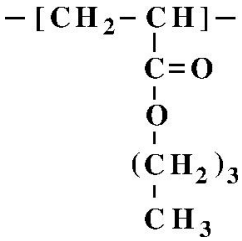

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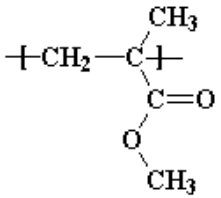

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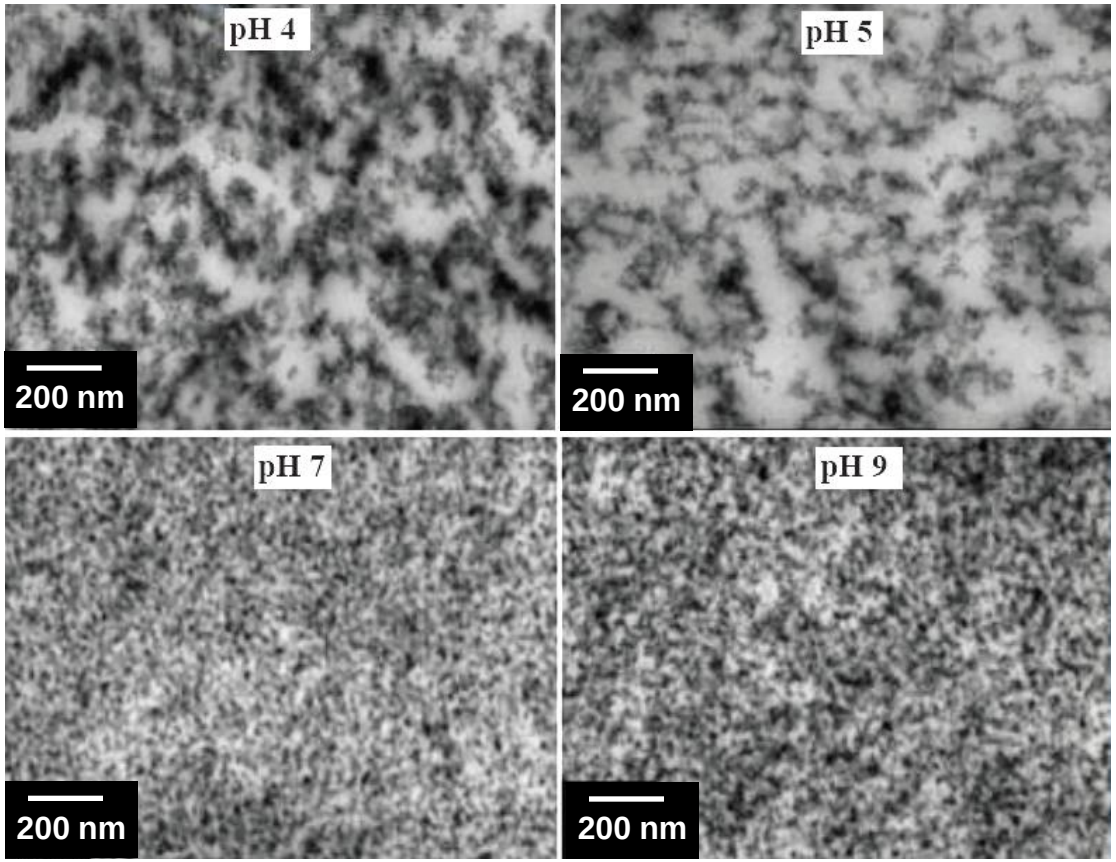


[M. TATOU, PhD thesis, Montpellier, (2010)]

TEM (120 kV)

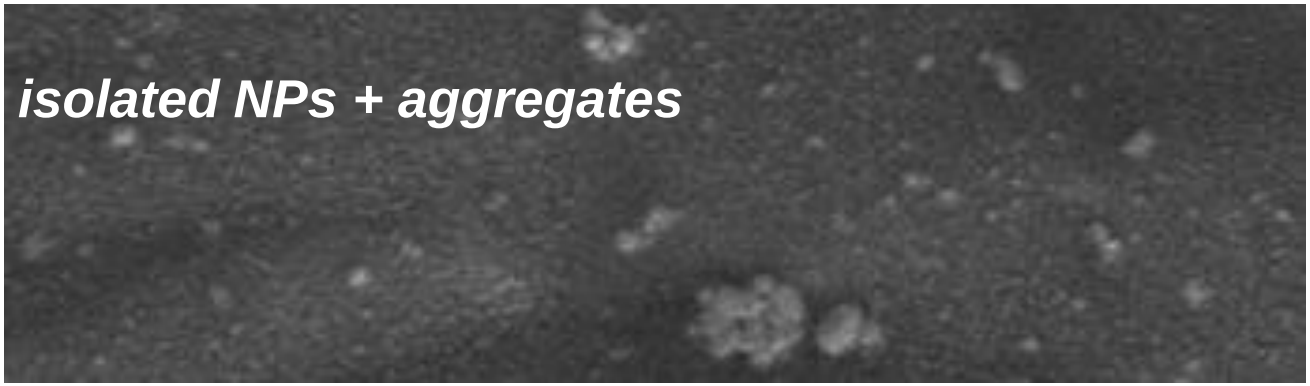
I. Materials and Techniques

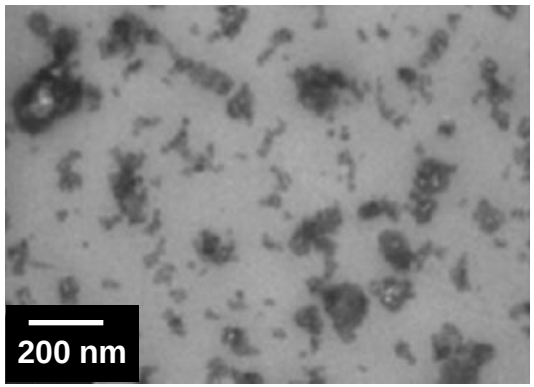
PMMA/PBuA 1% SiO_2, *PH5*

SEM (1kV, cryo-fracture)

[M. TATOU, (2010)]

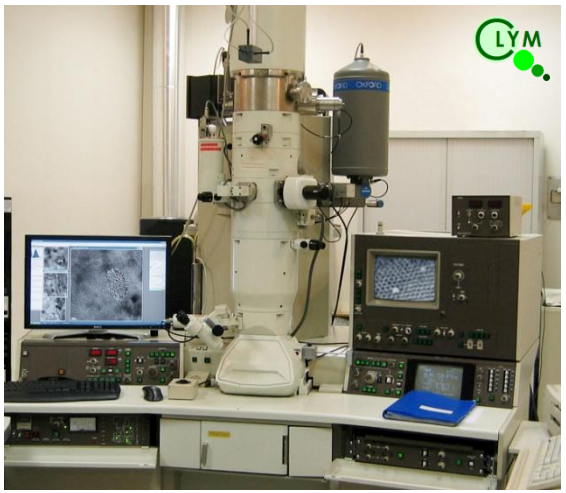
TEM (120 kV)





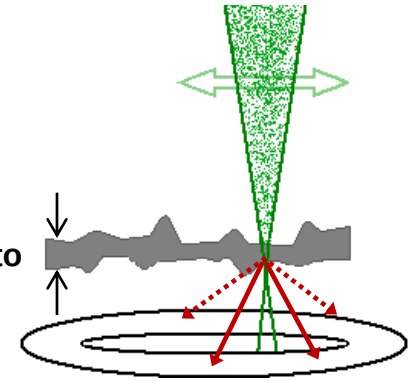
ZEISS Nvision 40
Tomo. FIB

FEI XL30 *30 kV*
Tomo 'STEM' ESEM



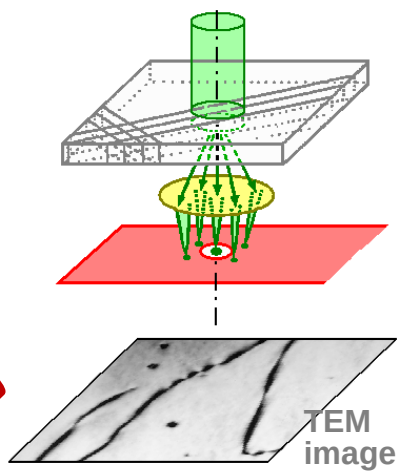
JEOL 2010F *200 kV*
Tomo. TEM-HAADF

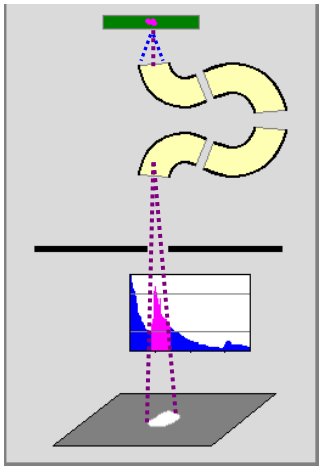
(low-voltage STEM :
Transmission mode in a SEM)

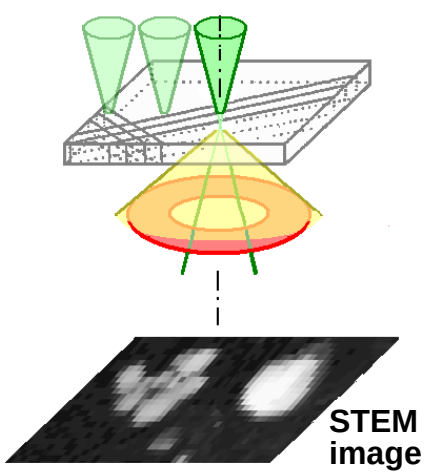


TEM thin foil *or* up to a few µm

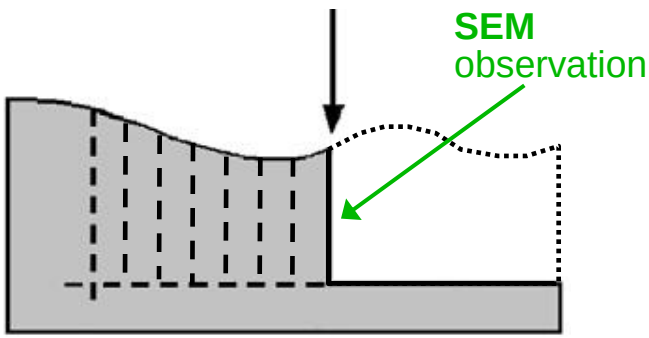
Conventional TEM | ***Energy-Filtered TEM*** | ***High Angle Annular Dark Field***



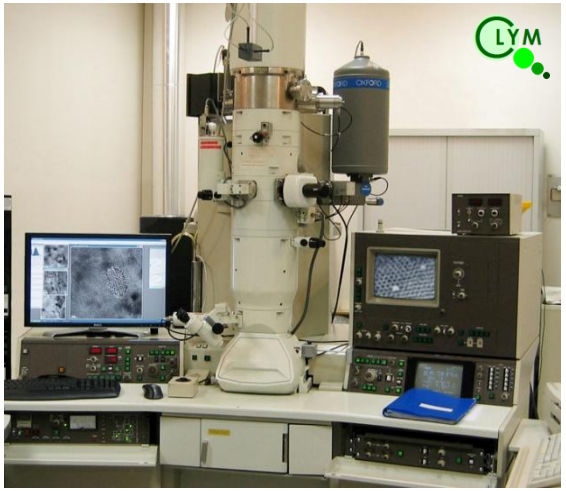




'slice & view' in a FIB



FEI **XL30** ***30 kV***
Tomo 'STEM' ESEM

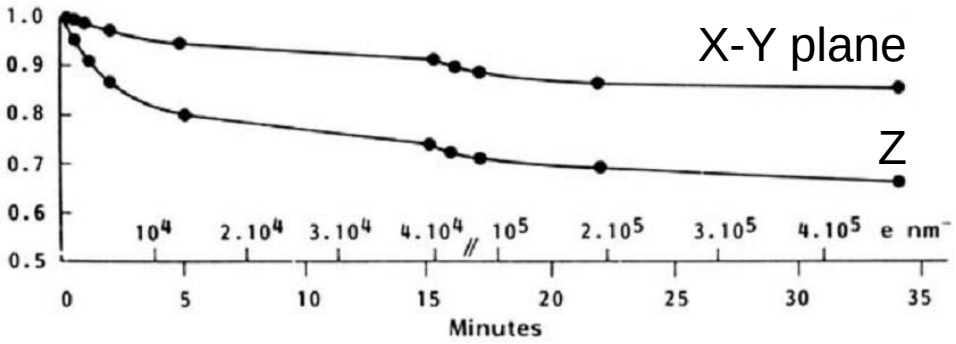


JEOL **2010F** ***200 kV***
Tomo. (EF)TEM-HAADF

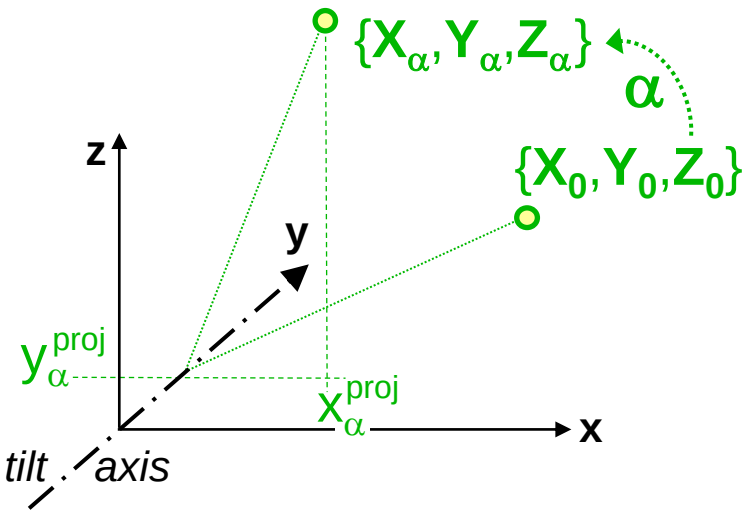
II. Polymers and charged particles

Polymers don't like charged particles!

II.1 The shrinkage effect



[P.K. LUTHER, chap. 1 in *Methods for Three-Dimensional Visualization of Structures in the Cell*, Springer (2006)]



- ***Rk.: shrinkage measurement: see 'late' poster* Y. LIU et al.**

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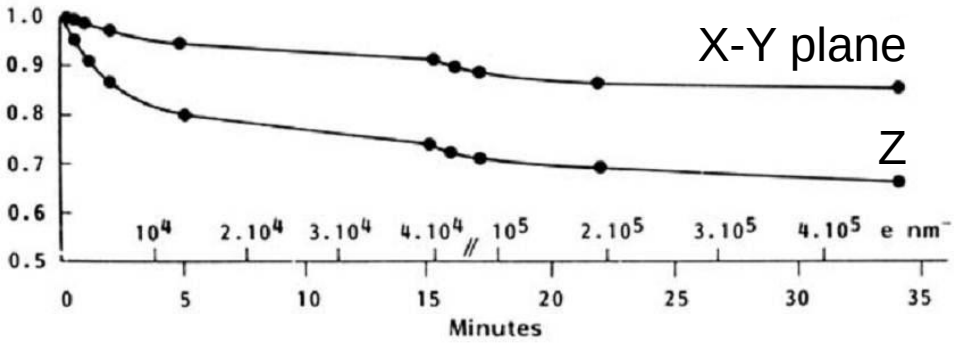

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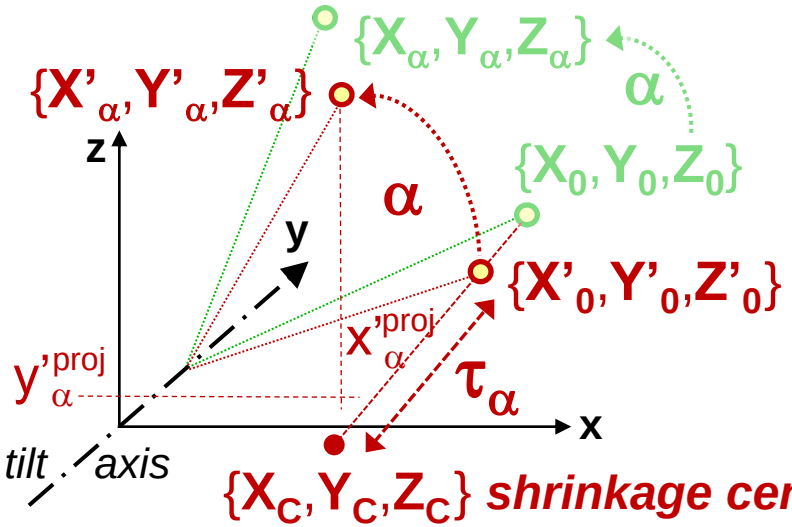

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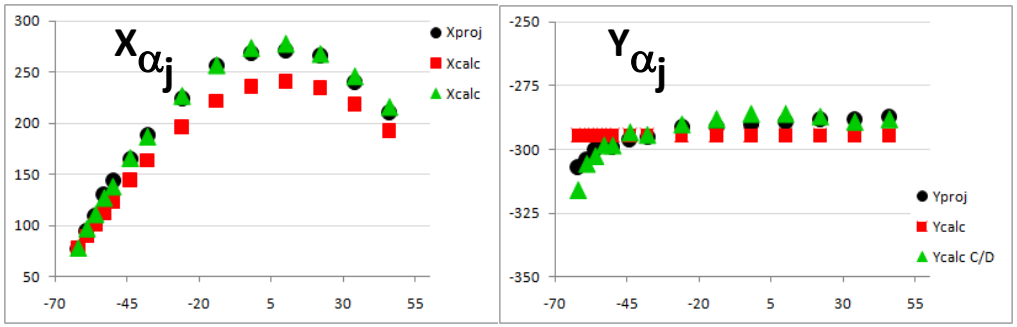
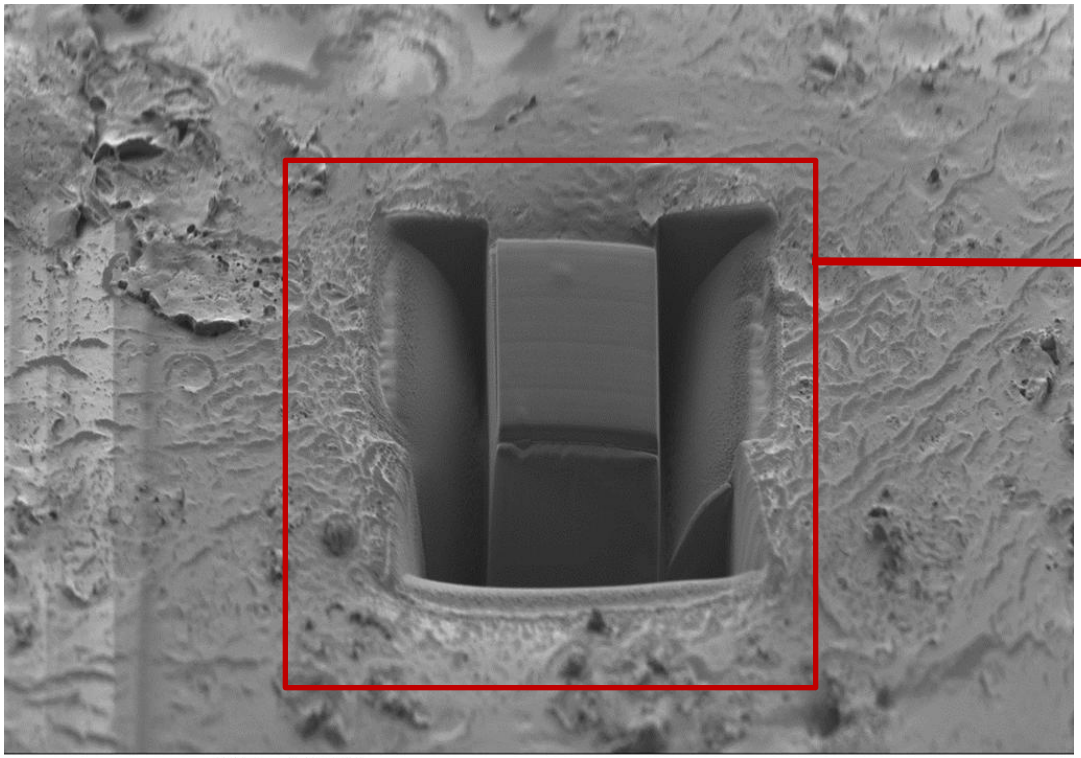
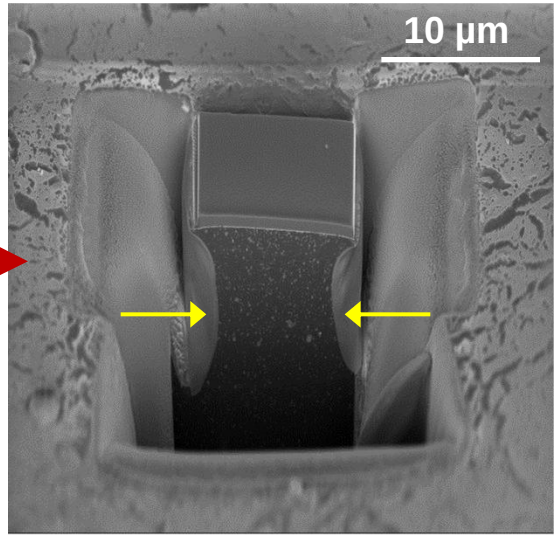
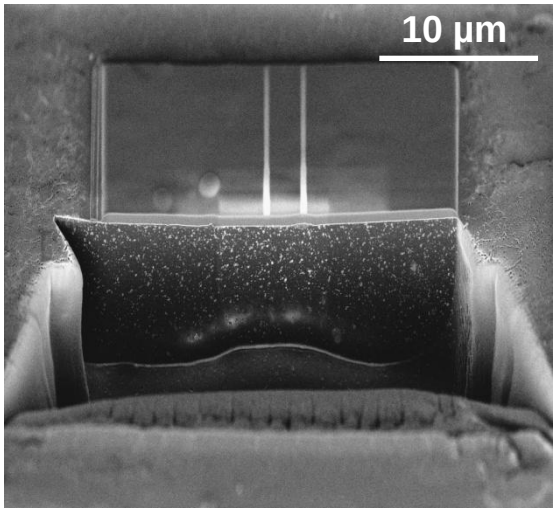


Shrinkage during FIB observation PMMA/PBuA 1% SiO_2, *PH5*



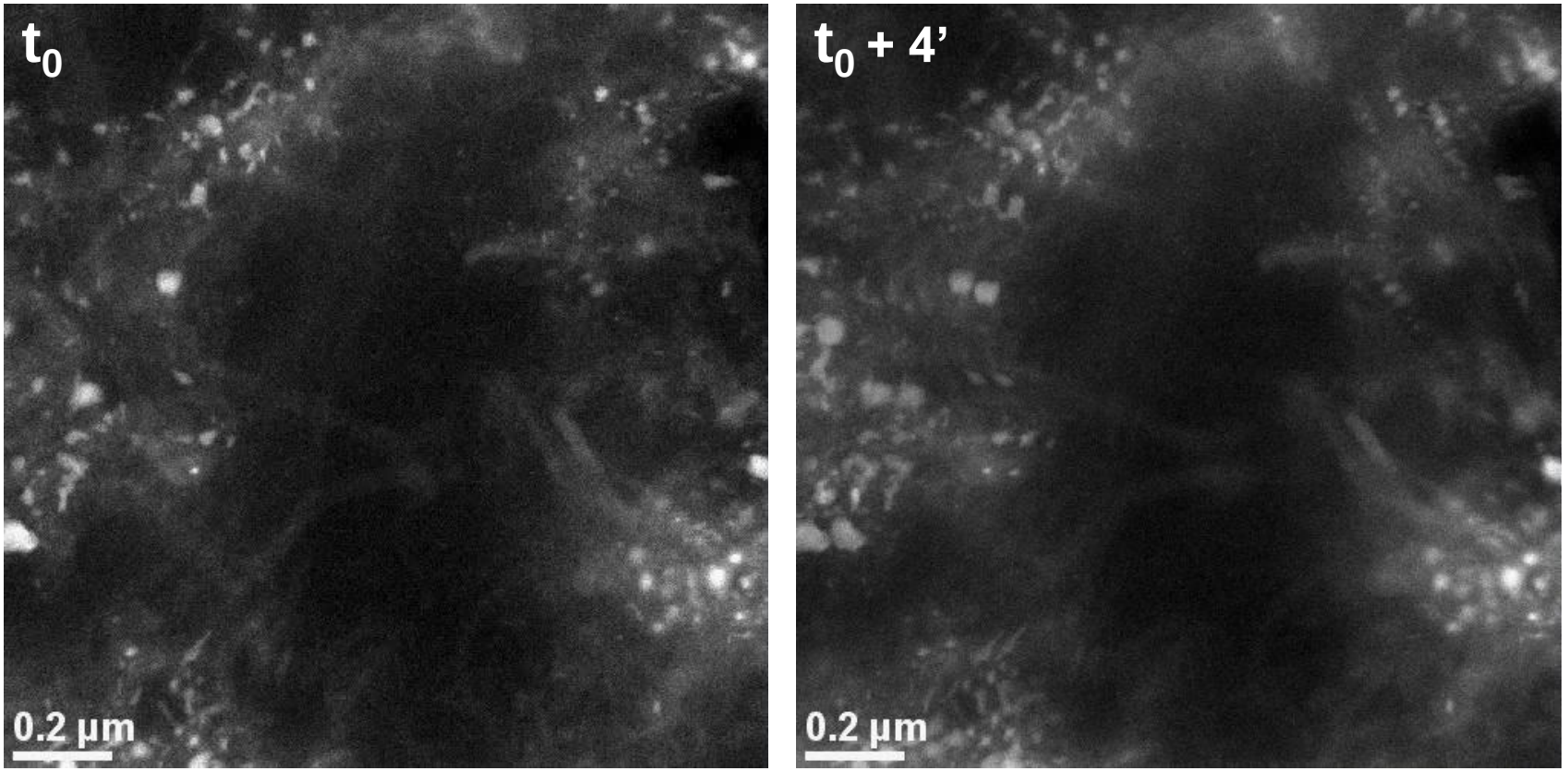




adopted geometry

Shrinkage during TEM observation

CNTs@polymer - Poly(**S**tyrene co-**Bu**tyl **A**crylate) **P(S-BuA) - nanocomposite**



● ***See communication* Y. LIU et al.**

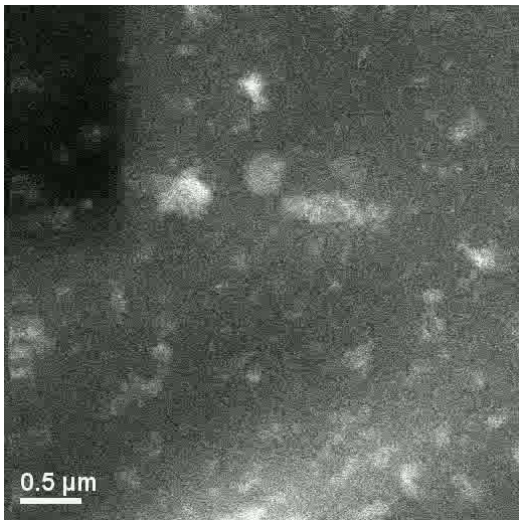
II. Polymers and charged particles

Polymers don't like charged particles!

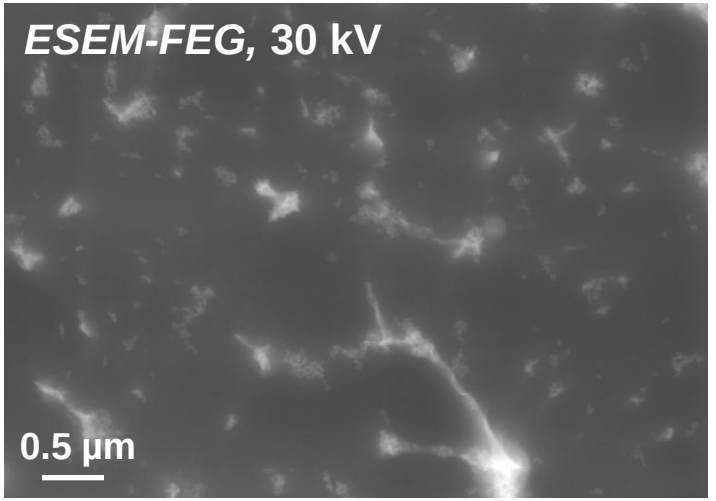
II.2 Electron-induced *mass-loss*

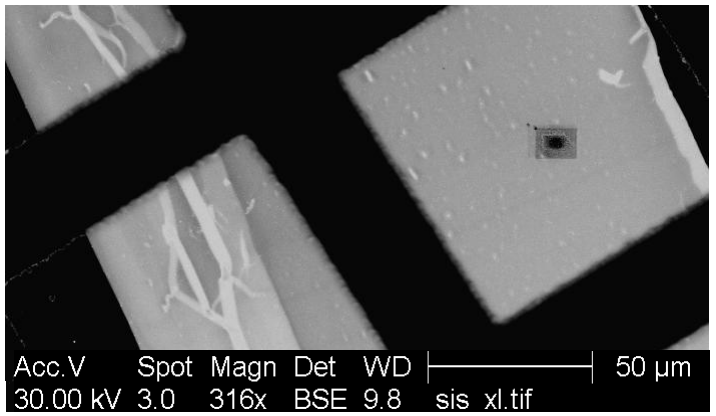
PMMA/PBuA 1% SiO_2, *PH5*

TEM 200 kV



STEM-HAADF
speed x2



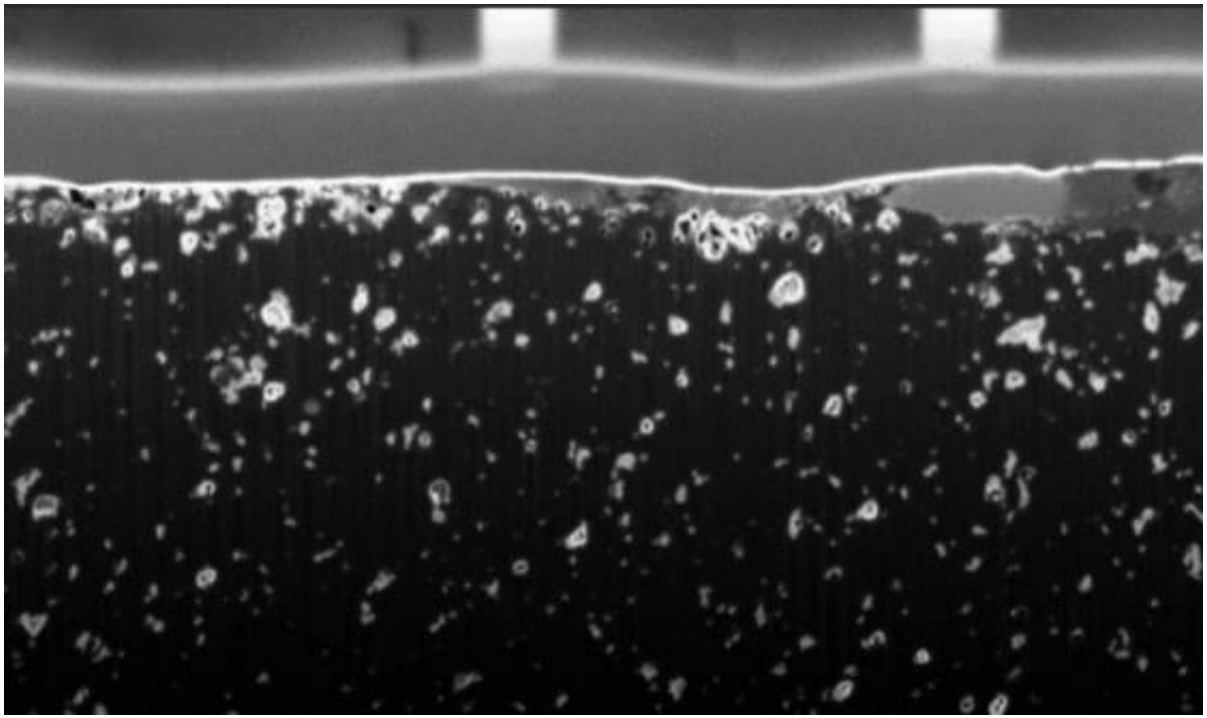


STEM in SEM

III. A Tri-3D approach of polymer nanocomposites

III.1 FIB tomography

PMMA/PBuA 1% SiO_2, *PH5*



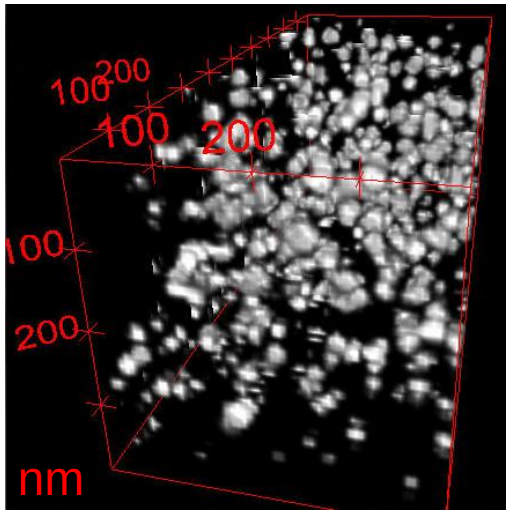
Typical sequence and depth/slice: 500 slices, 6 (to 10) nm

Note: life / automatic correction of DRIFT

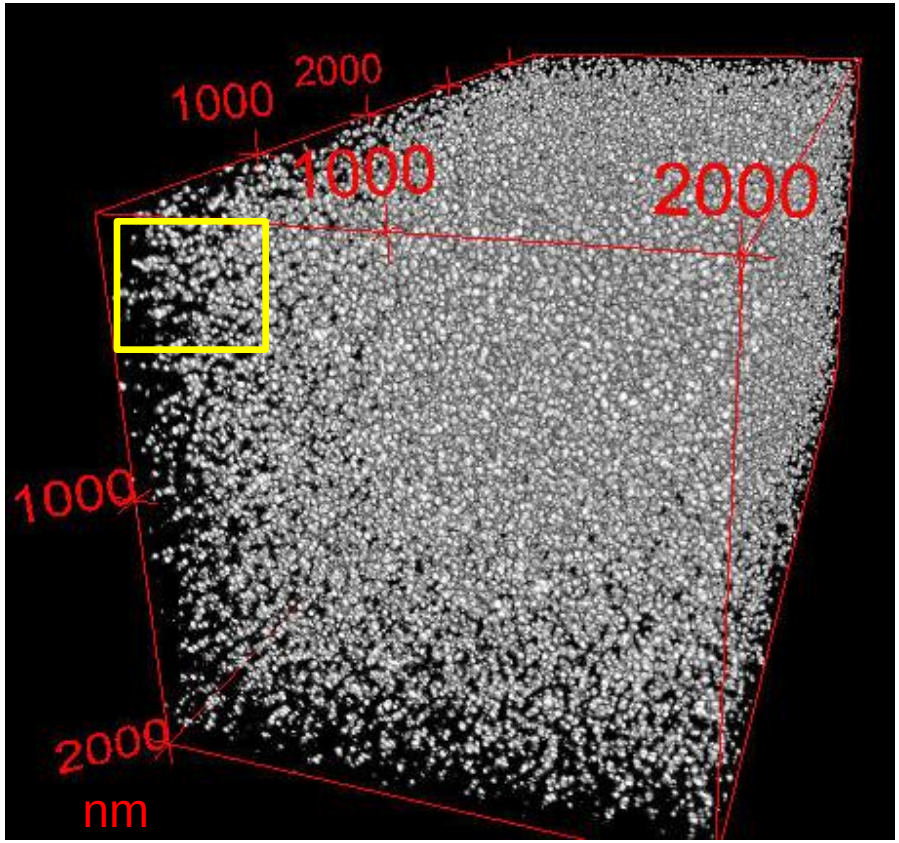
application (ZEISS API):

VB6 programming + Stackreg [P. Thévenaz et al., *IEEE Trans. on Image Proc.* 7, (1998) 27] procedure in **FIJI** (http://fiji.sc/wiki/index.php/Fiji)

- ***See poster* H. YUAN et al.**



100^3 voxels



segmented / erosion / dilation

500*500*454 voxels

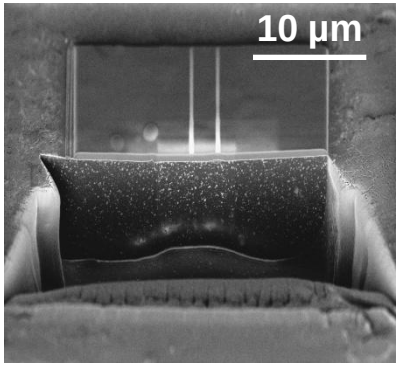
voxel 4*4*10 nm

$\mathcal{F}_{SiO2} = V_{SiO_2} / V_{total} \approx 4.9\%$

Expected value:
1 % [M. TATOU, PhD thesis, **(2010)**]

• Effect of the shrinkage?

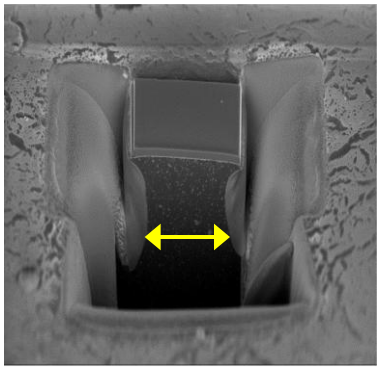
Mostly avoided in FIB…



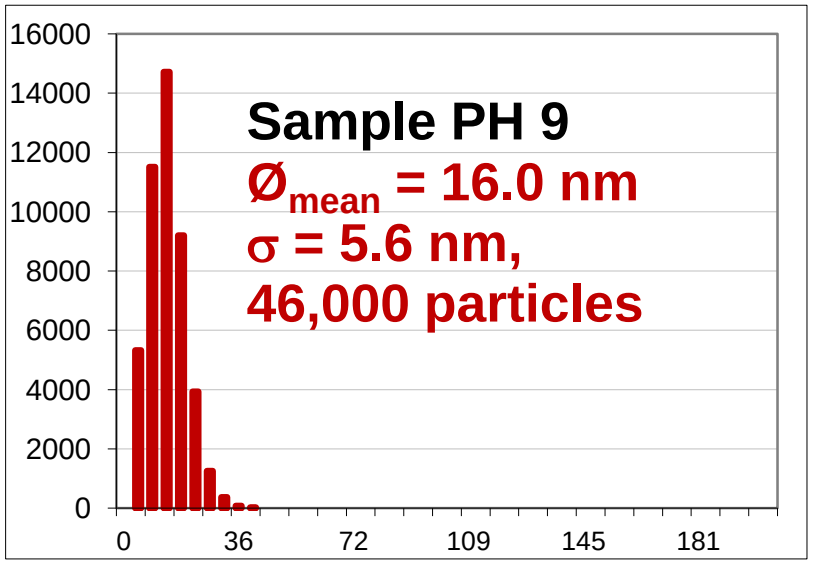
and effect less than ≈ 25%

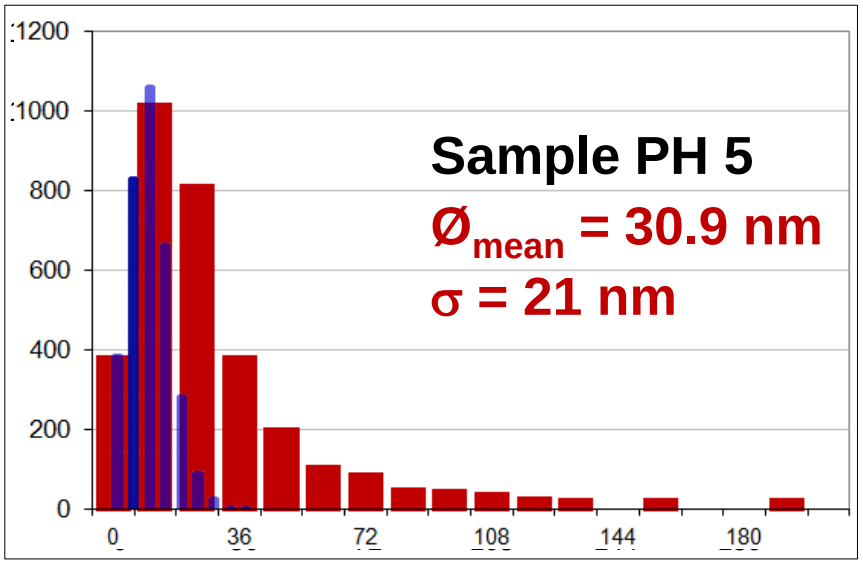
$\mathcal{F}_{SiO_2} \approx$ ~~4.9%~~ ≈ 3.6%

Expected value 1 %

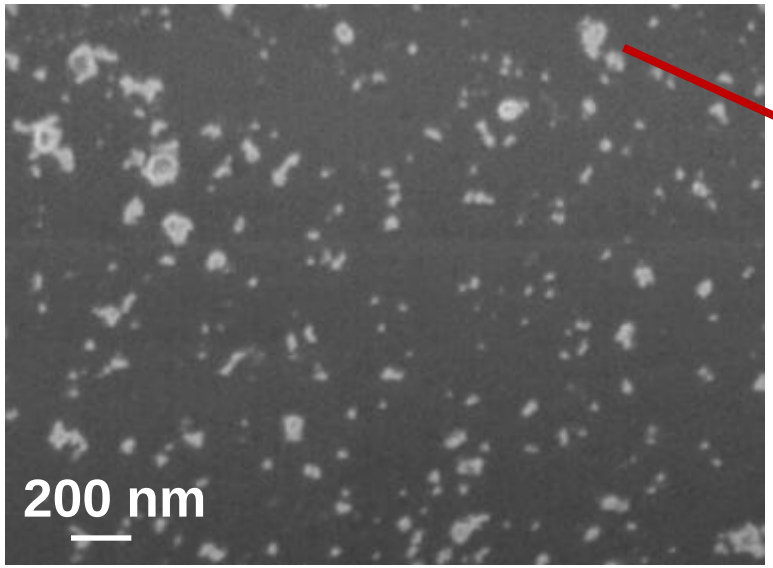


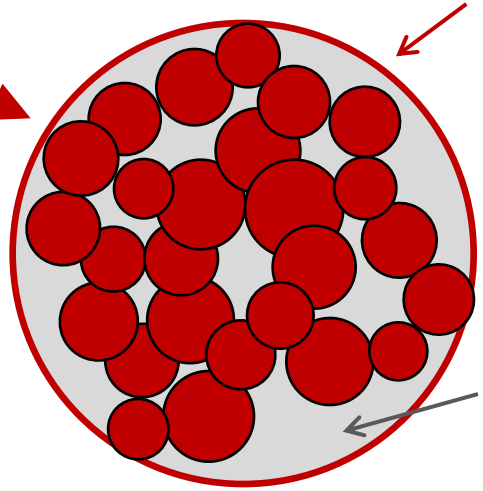
• Structure of the particle aggregates?





SEM-FIB, 1 kV





apparent size of aggregates as revealed in SEM/FIB $(\varnothing^{i}_{SiO_2})$

hidden matrix $(1-\tau^{i}_{SiO_2})$

$$\mathcal{V}^{apparent}_{SiO_2} = \sum 4\pi(\varnothing^{i}_{SiO_2}/2)^3/3 \quad \text{and} \quad \mathcal{F}^{apparent}_{SiO_2} = \mathcal{V}^{apparent}_{SiO_2} / \mathcal{V}_{total}$$

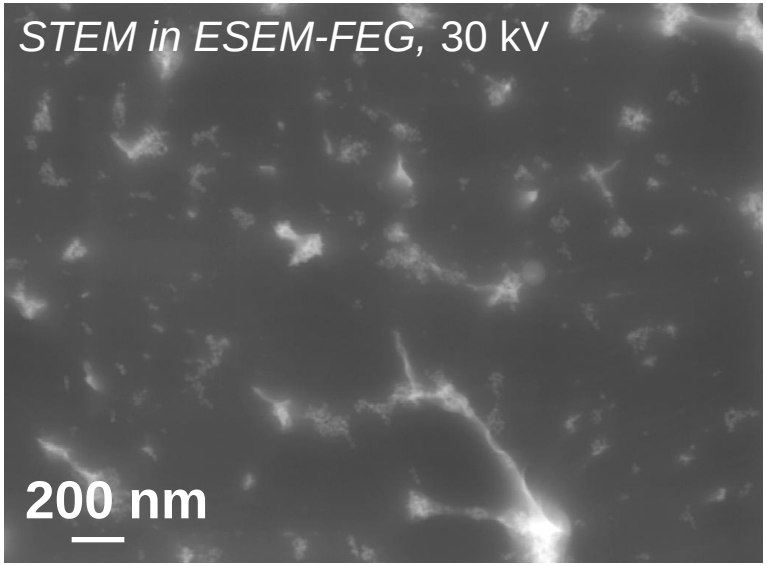
$$\mathcal{V}^{corrected}_{SiO_2} = \sum \tau^{i}_{SiO_2} 4\pi(\varnothing^{i}_{SiO_2}/2)^3/3 \quad \text{and} \quad \mathcal{F}^{corrected}_{SiO_2} = \mathcal{V}^{corrected}_{SiO_2} / \mathcal{V}_{total}$$

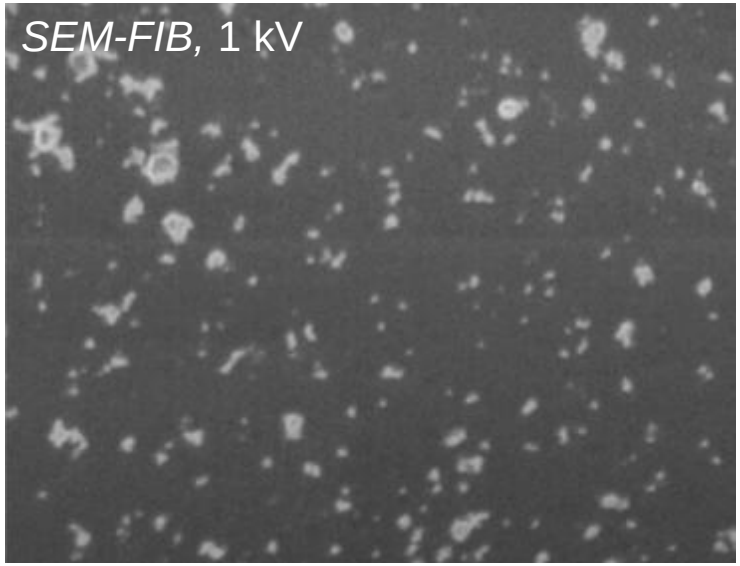
- **NEED for higher resolution** to measure the ratio of *hidden matrix*

- tilting tomography in TEM

- tilting tomography in LOW VOLTAGE SEM?

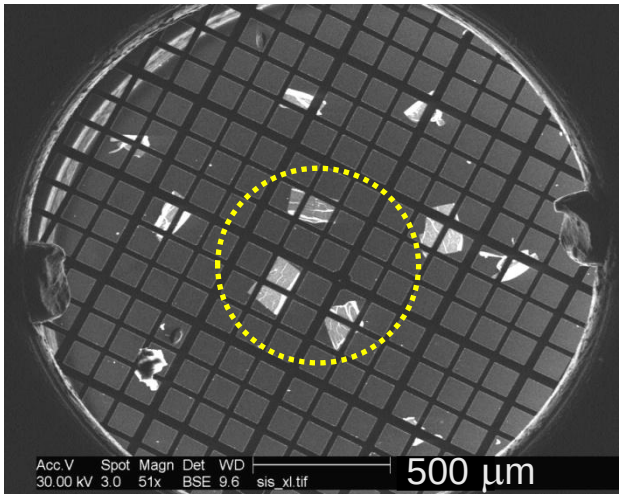
III.2 Tilting tomography in LOW VOLTAGE STEM in a SEM

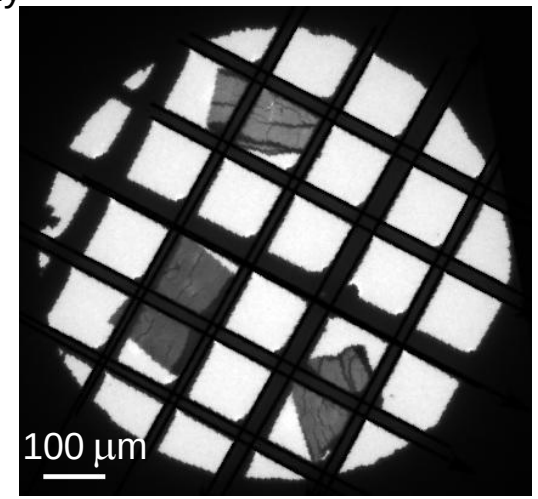




ultramicrotomy
(50-200 nm)

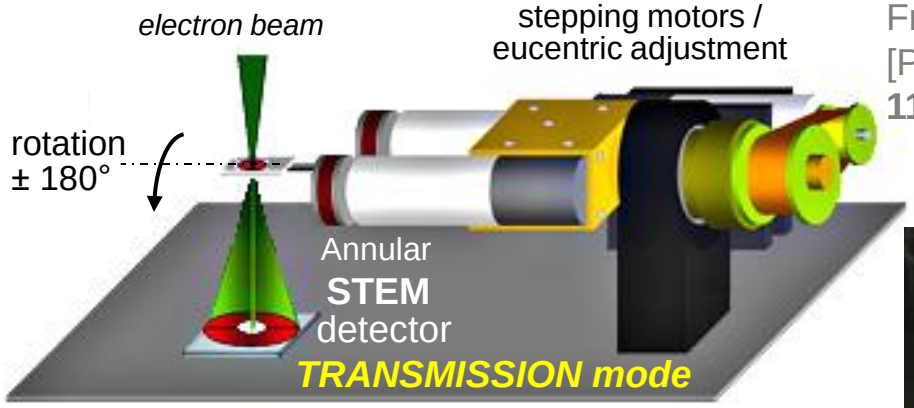
STEM *mode in a SEM*





TEM *BF mode*

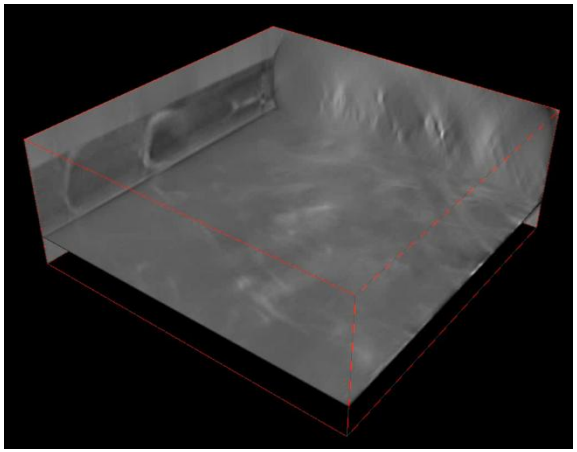
FEI XL30 *30 kV*
ESEM

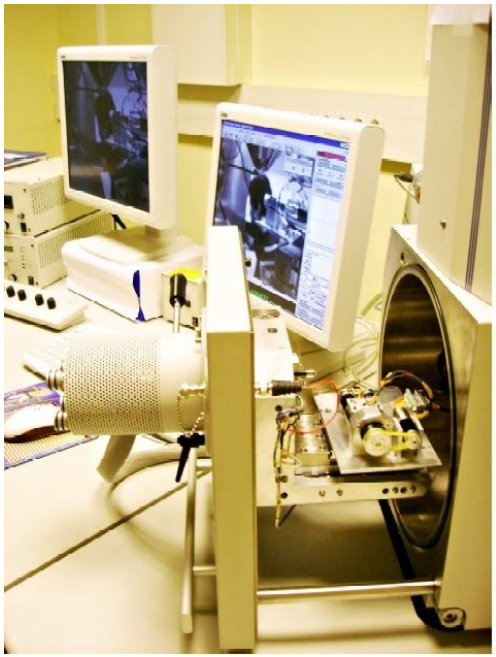


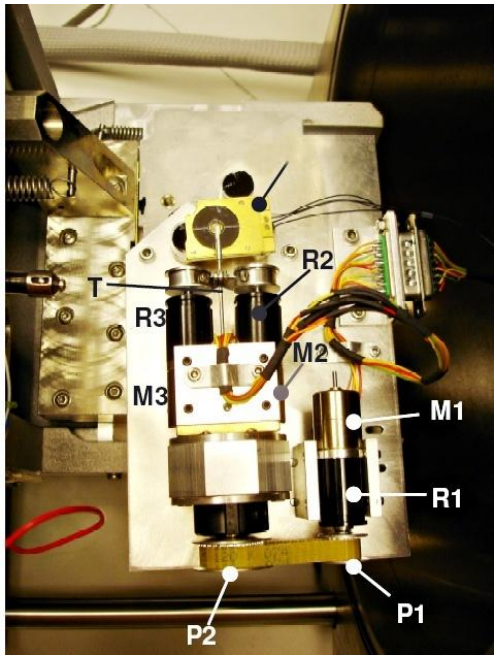
French PATENT FR06-09-708, (2006)
[P. JORNSANOH et al., *Ultramicrosc.*, **111**, (2011), 1247-1254]

200 nm

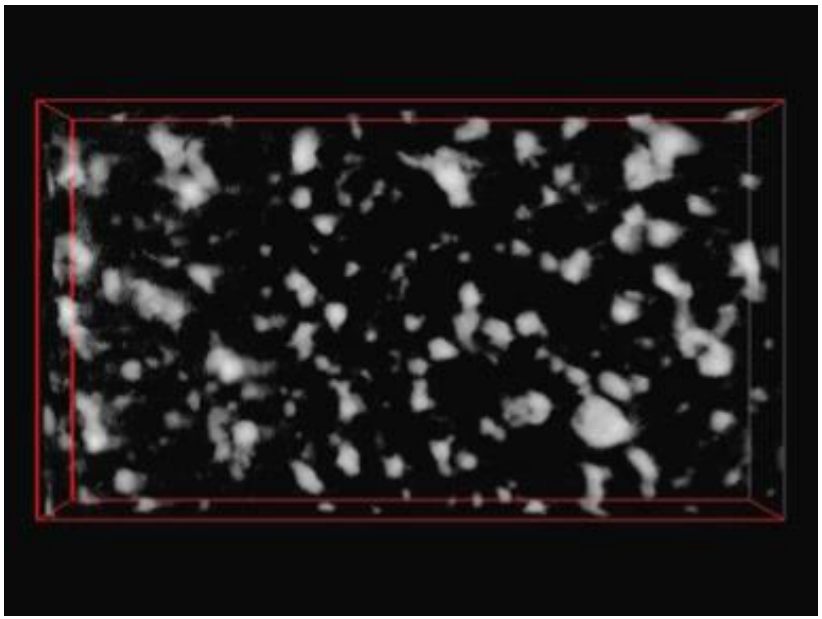
CNTs@P(S-BuA)



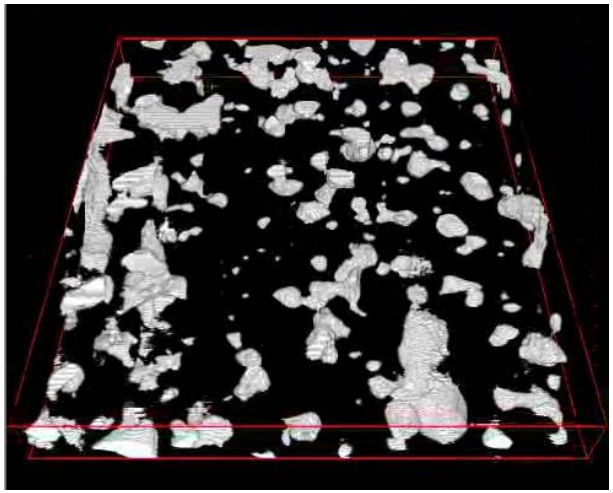




PMMA/PBuA 1% SiO_2, *PH5*



1 µm

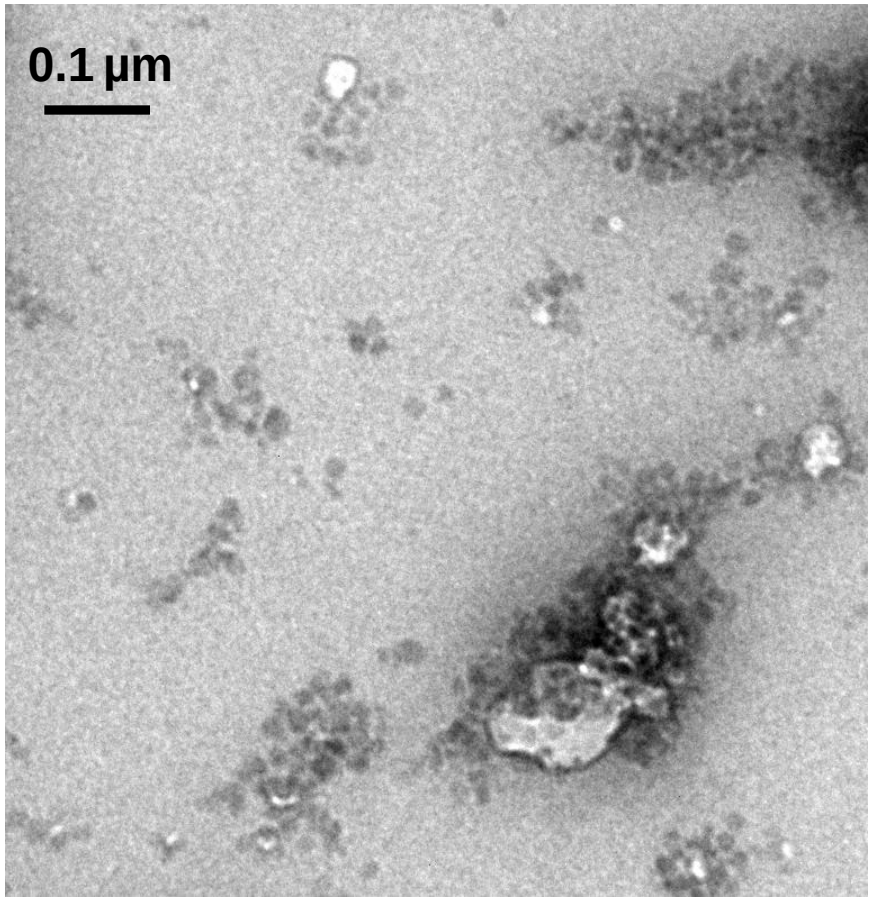


Reconstruction from a tilted serie +40° / -40°, step 5°

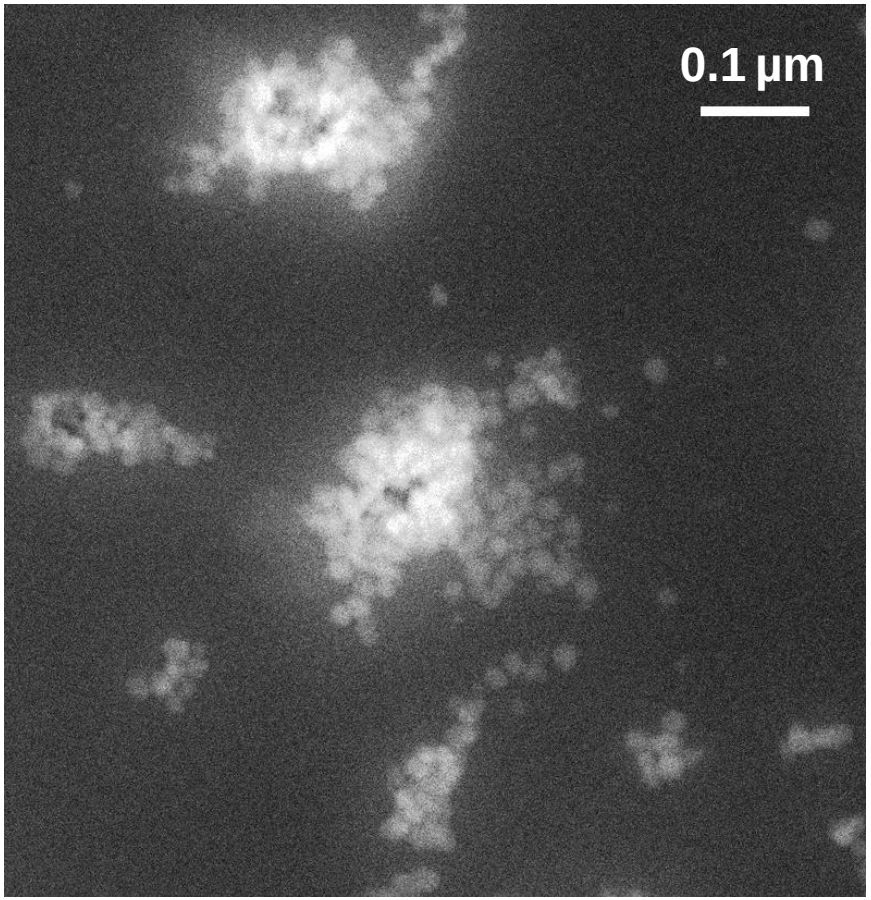
- **NO improvement in the 3D resolution (internal structure of aggregates)**

III.3 Tilting tomography in TEM (200 kV)

TEM BF mode

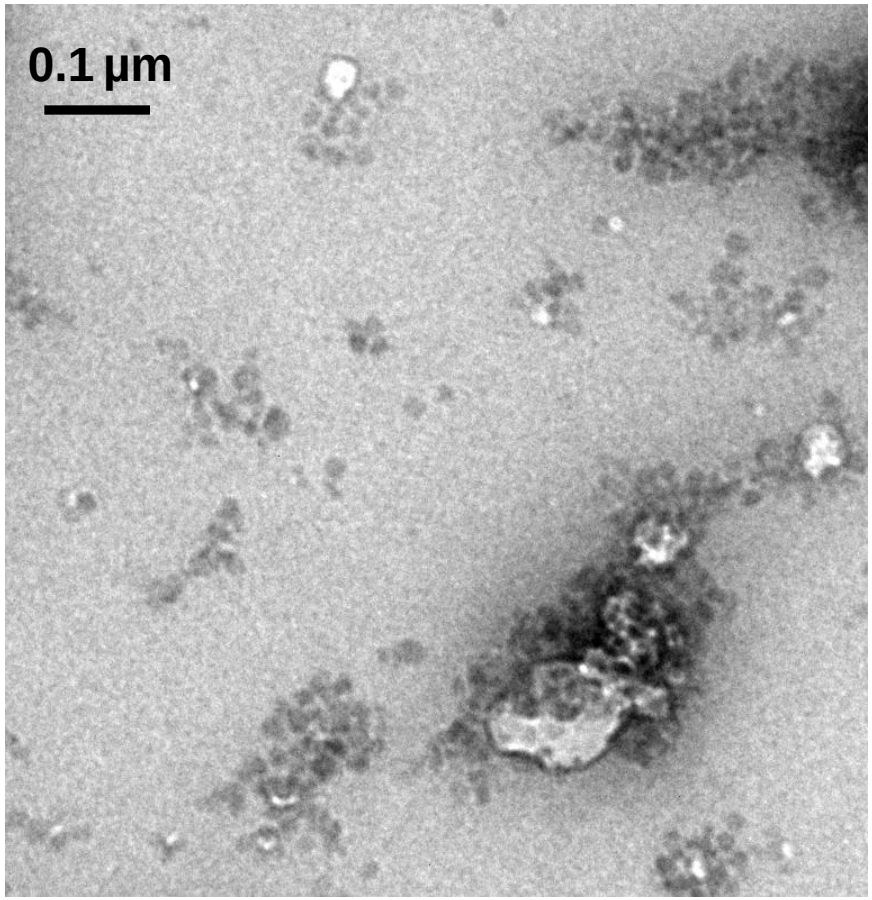


STEM-HAADF



III.3 Tilting tomography in TEM

TEM BF mode

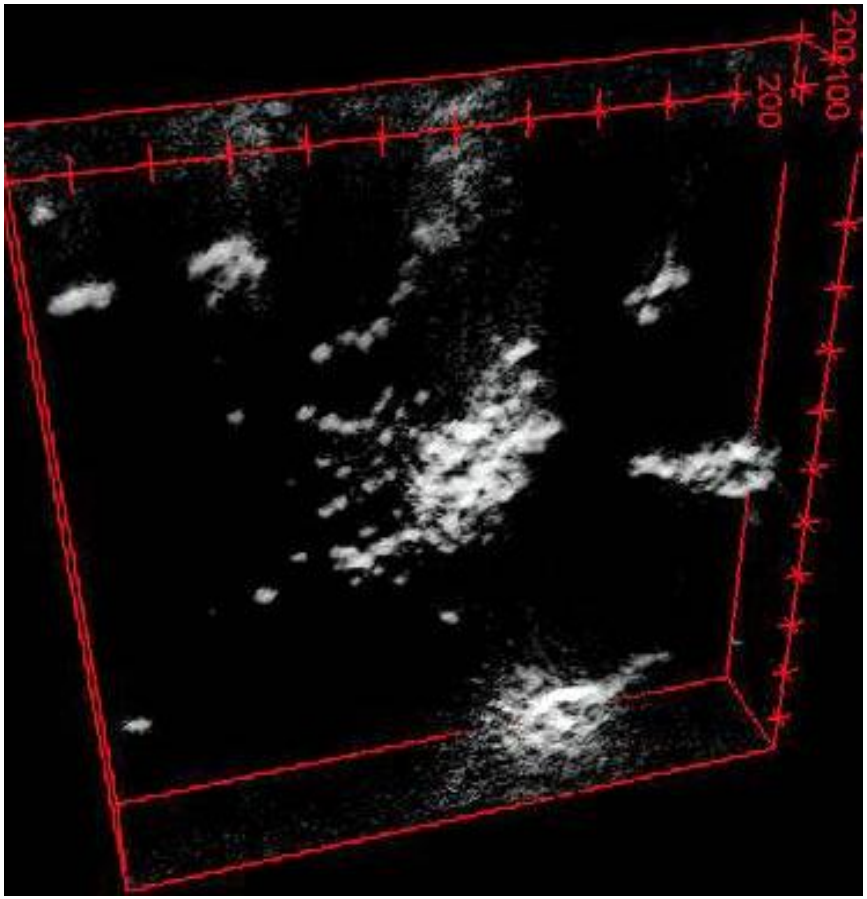


CTEM
speed x2

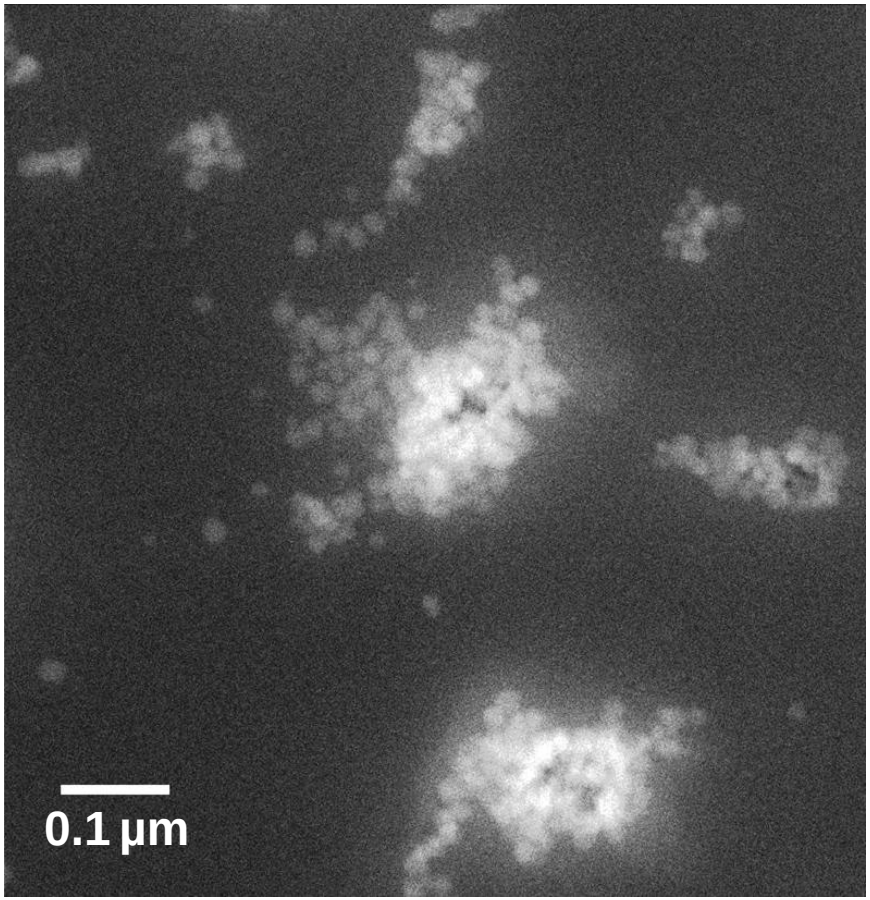
irradiation-induced cavitation in aggregates

III.3 Tilting tomography in TEM

Tilted series , -58° / 30°, step 4°



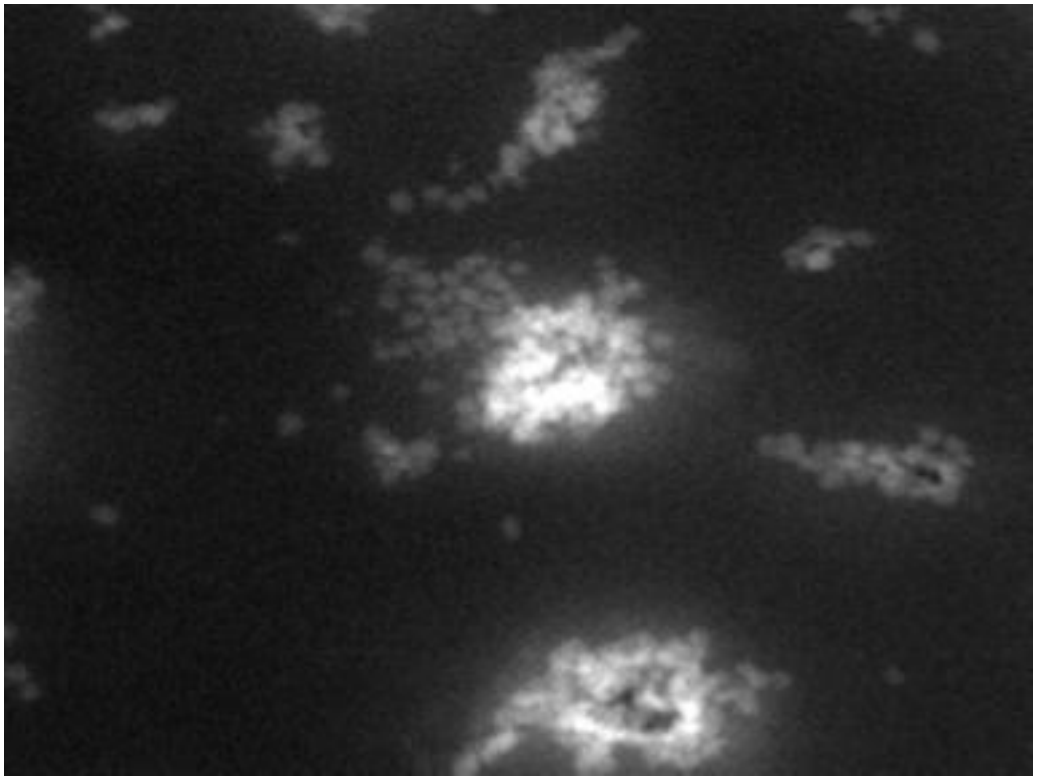
STEM-HAADF

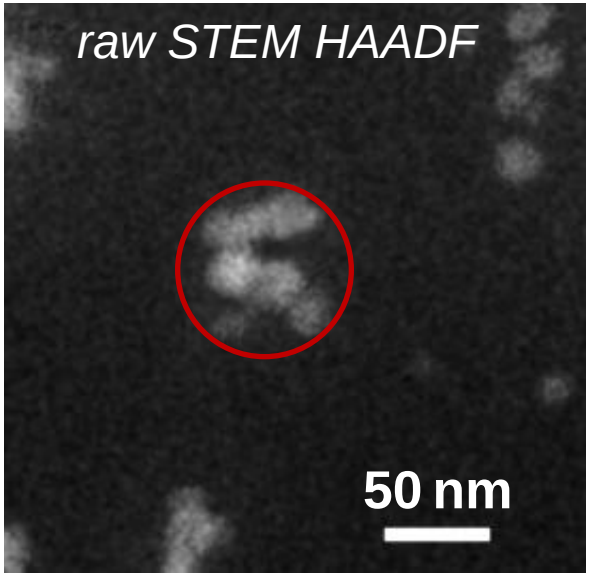


III.3 Tilting tomography in TEM

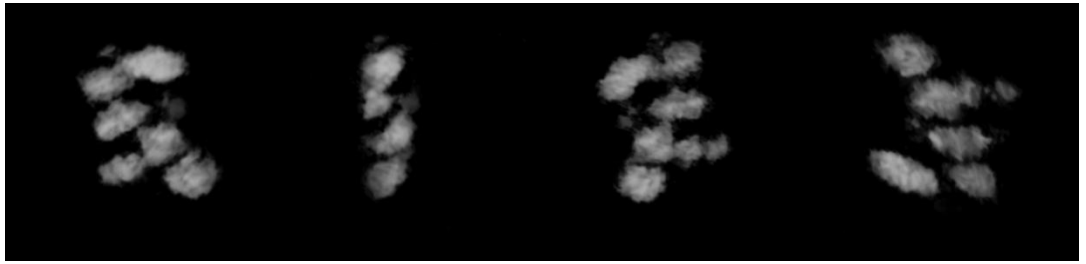
Tilted series , -58° / 30°, step 4°

0.1 µm

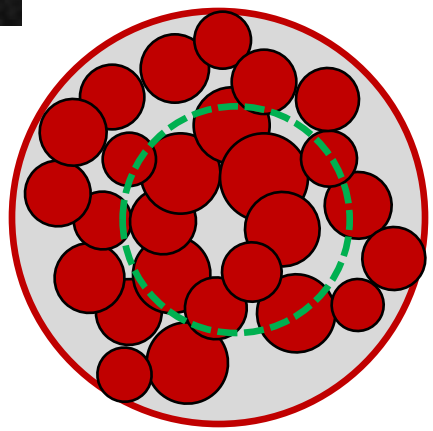


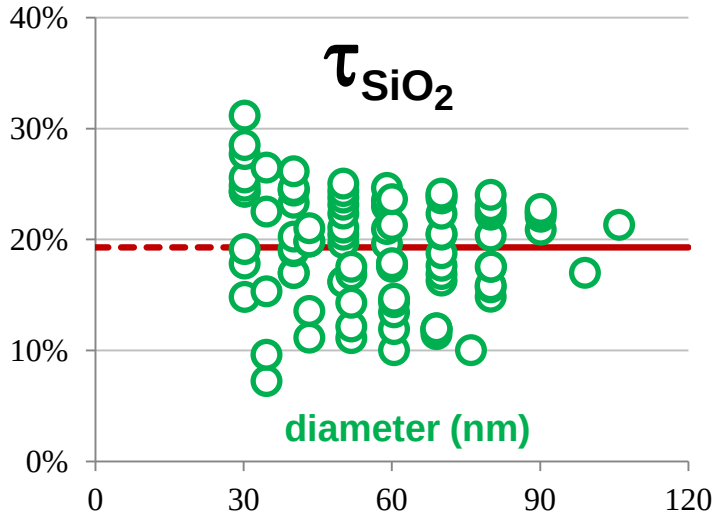


from reconstructed volume



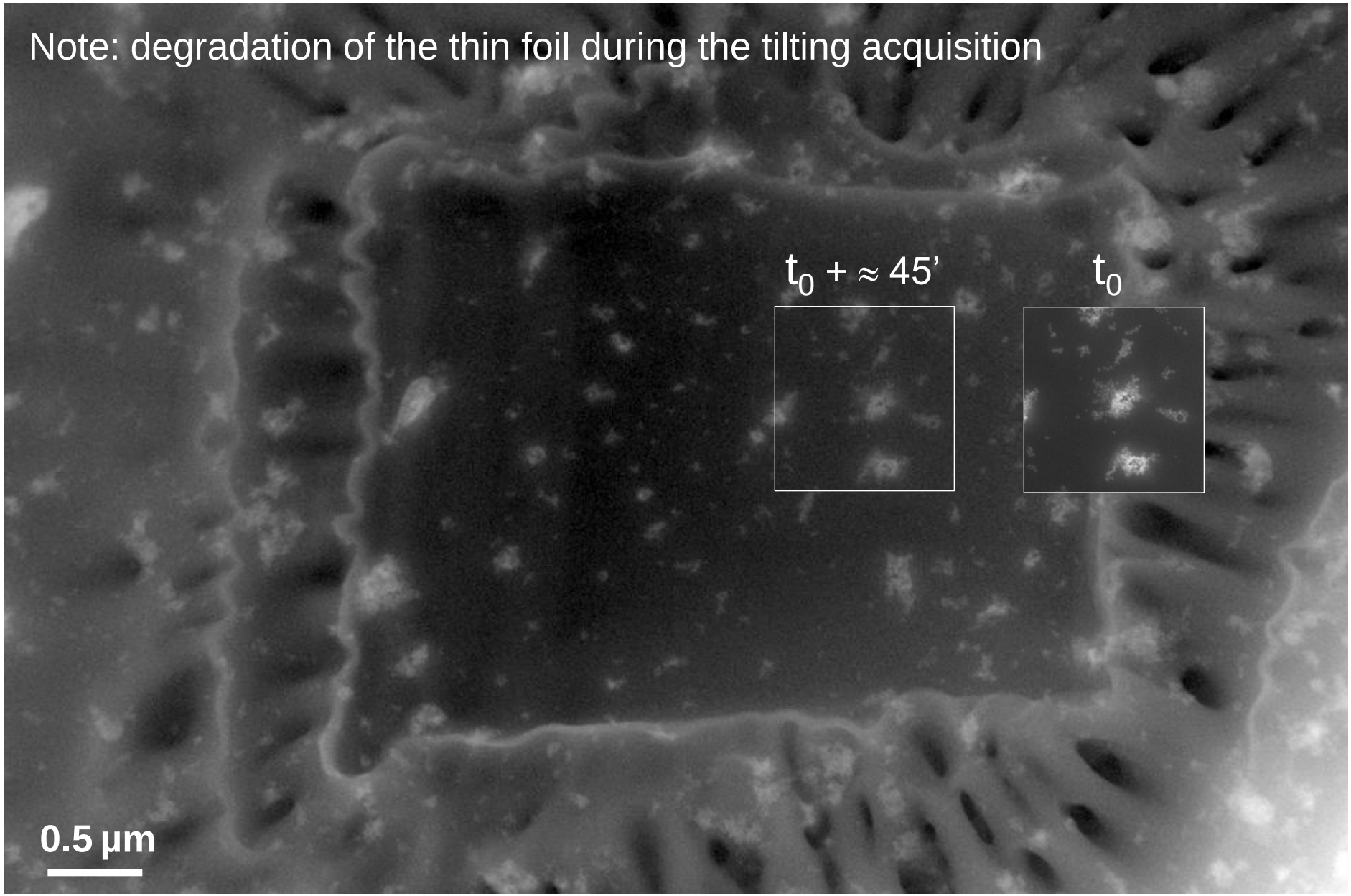
- **Clear evidence for a low density τ_{SiO_2} of NPs in aggregates**





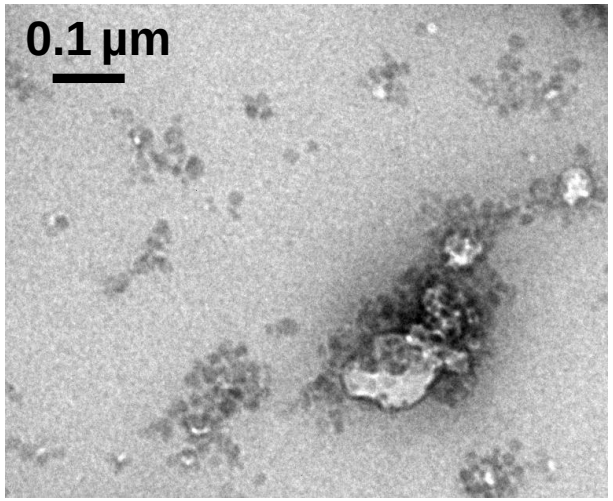
$$\tau_{SiO_2} \approx Cst^t = 20\% \pm 10\%$$

$$V_{SiO_2}^{corrected} \approx \tau_{SiO_2} V_{SiO_2}^{apparent} \text{ and } F_{SiO_2}^{corrected} = \tau_{SiO_2} F_{SiO_2}^{apparent} = 0.2 * 4.9\% \approx 1\% \pm 0.5\%$$


Note: degradation of the thin foil during the tilting acquisition
t_0 + ≈ 45'
t_0
0.5 µm

IV. Conclusion

- **For the chemists in polymer science: nucleation of voids within the aggegates…**



- **Interest of coupling tomographic techniques at different and complementary scales (FIB / (SEM) / TEM)**

- **Complements to this approach:**
  - **(i) communication Y. LIU** on TEM tomography of CNTs@P(S-BuA) polymer nanocomposites
  - **(ii) posters H. YUAN et al.** (live drift corrections in FIB 3D), **Y. LIU et al.** (quantification of shrinkage)

Please apologize for this unusual conclusion…

Agnès BOGNER-VAN DE MOORTELE
our colleague, assistant–professor (MATEIS lab.)
our co-author,
our FRIEND

passed away on Tuesday, February 28, just one week ago.
She was only 35.
She has been fighting during 2 years against an unfair illness, with her youth, her kindness, her simplicity.

It is just too sad.

Her husband, Bertrand VAN DE MOORTELE, is also *our colleague, our co-author, our FRIEND.*

We are just with him.

ACKNOWLEDGEMENTS

- plateform **CLYM** at ***Lyon***
  for access to ZEISS NVision40, FEI XL30, JEOL 2010F microscopes

- **Thierry DOUILLARD, Nick BLANCHARD, Armel DESCAMPS-MANDINE** for taking care of the Nvision 40 FIB;
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