

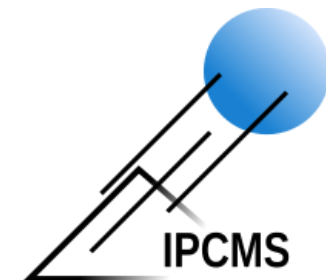


Liquid-Phase Transmission Electron Microscopy : Principles and Applications

Charles Sidhoum

PhD Student – IPCMS - Strasbourg

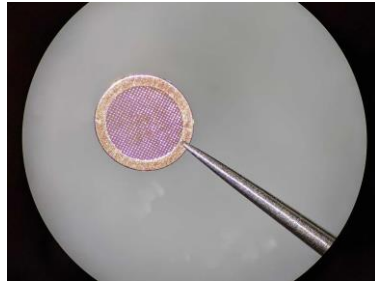
Characterization DAYS of GDR NINO Strasbourg, November 8-10, 2023
« From Standard to advanced characterization techniques »



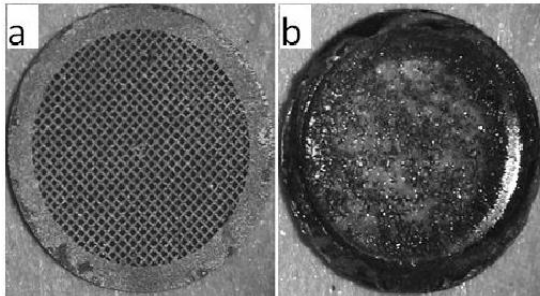
TEM column is under ultra-high vacuum

↔ samples have to be stable in these conditions

Conventional TEM (*Ex-situ*)

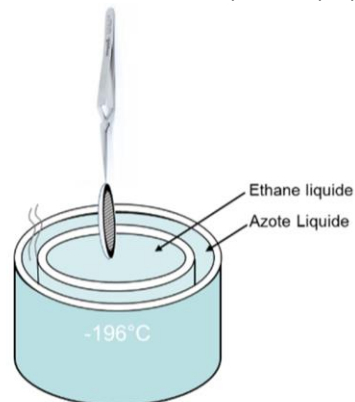


Embedded sample



Rao, Duggi V. Sridhara et al. "TEM specimen preparation techniques." (2010).

Cryo - TEM



D. Ihiawakrim. Thèse de Doctorat, Université de Strasbourg (2019)

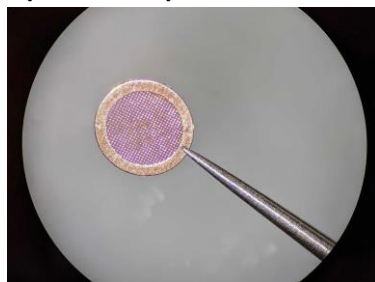
- Alteration of the sample
- No dynamic tracking
- Weak representativeness of certain phenomena

Why using LPTEM ?

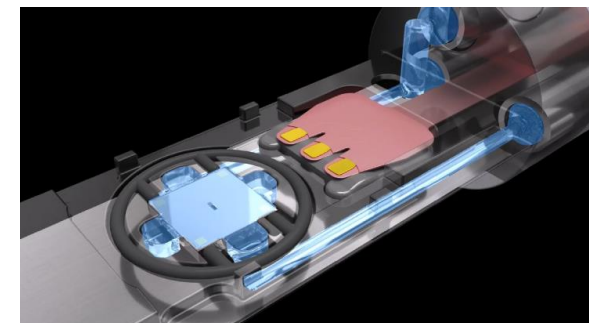
TEM column is under ultra-high vacuum

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Conventional TEM (*Ex-situ*)



Embedded sample

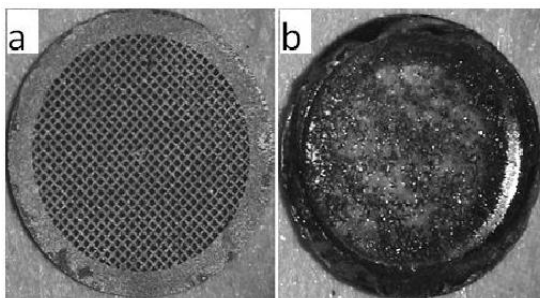


Liquid-Phase TEM



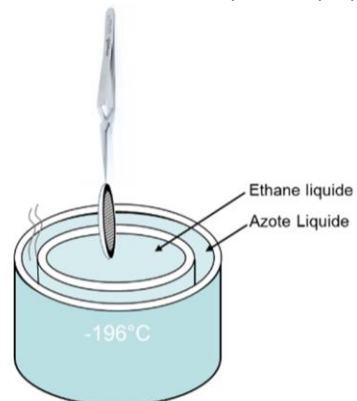
THE NANO-AQUARIUM: A NEW PARADIGM IN ELECTRON MICROSCOPY

Joseph M Grogan, Nicholas M Schneider, Frances M Ross, Haim H Bau

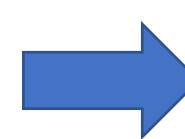
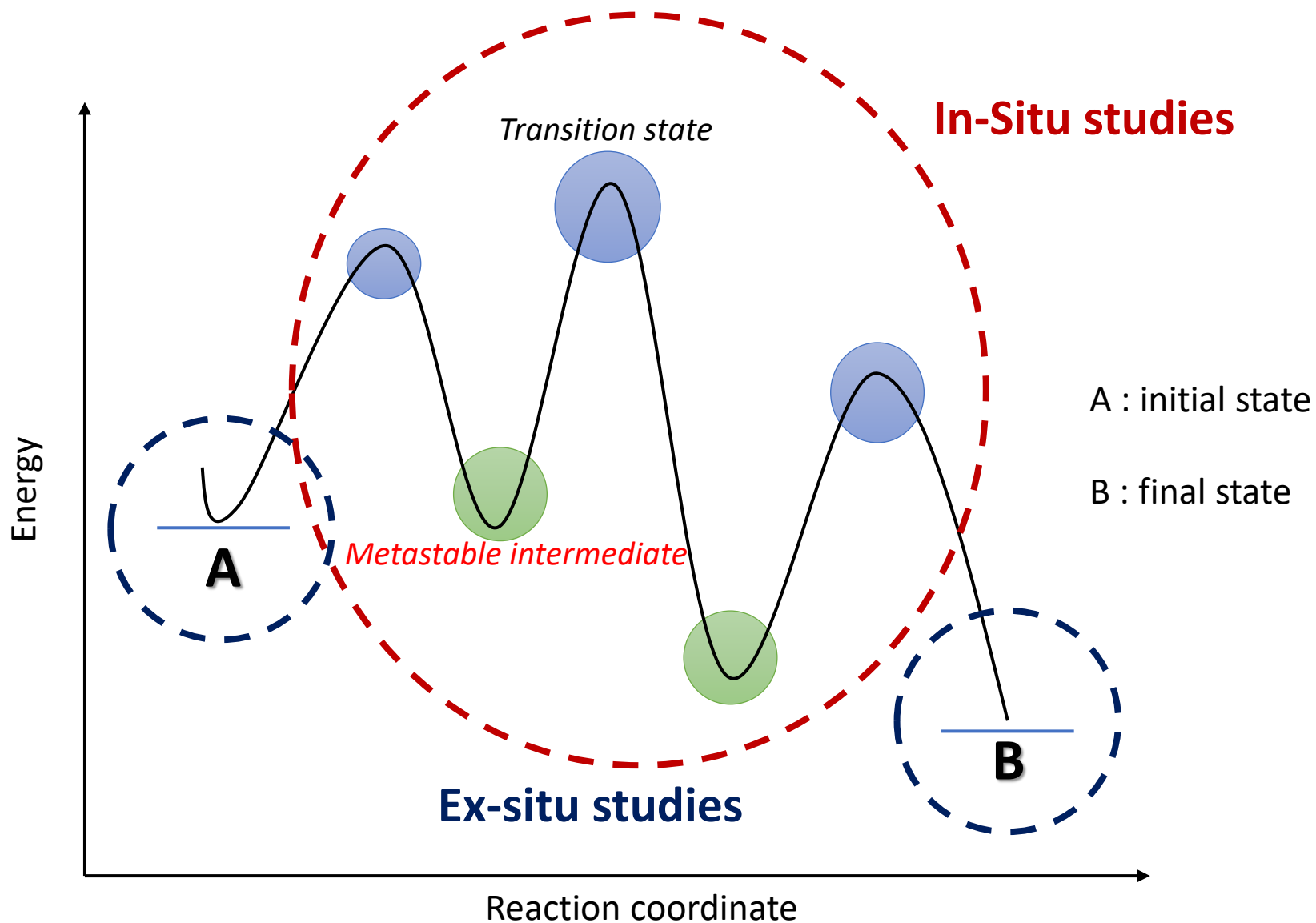


Rao, Duggi V. Sridhara et al. "TEM specimen preparation techniques." (2010).

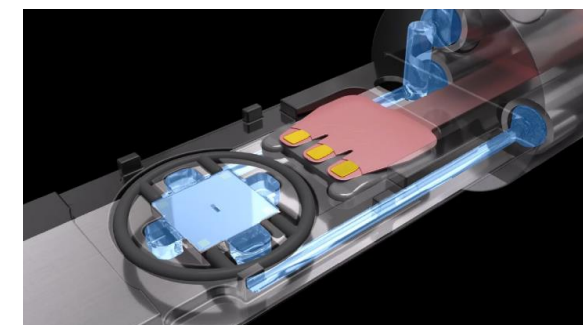
Cryo - TEM



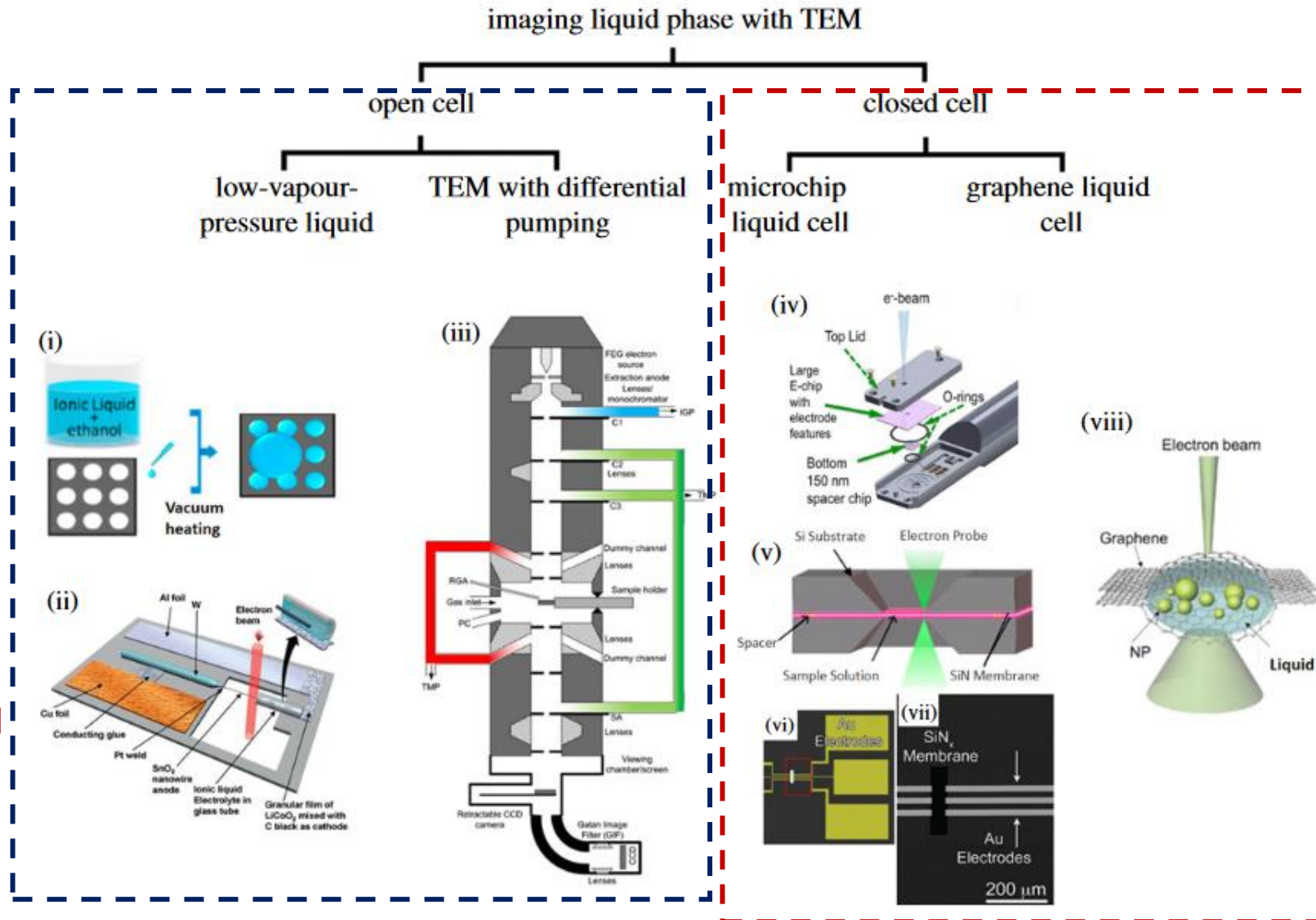
D. Ihiawakrim. Thèse de Doctorat, Université de Strasbourg (2019)



Need of dynamic tracking !



Liquid-Phase TEM

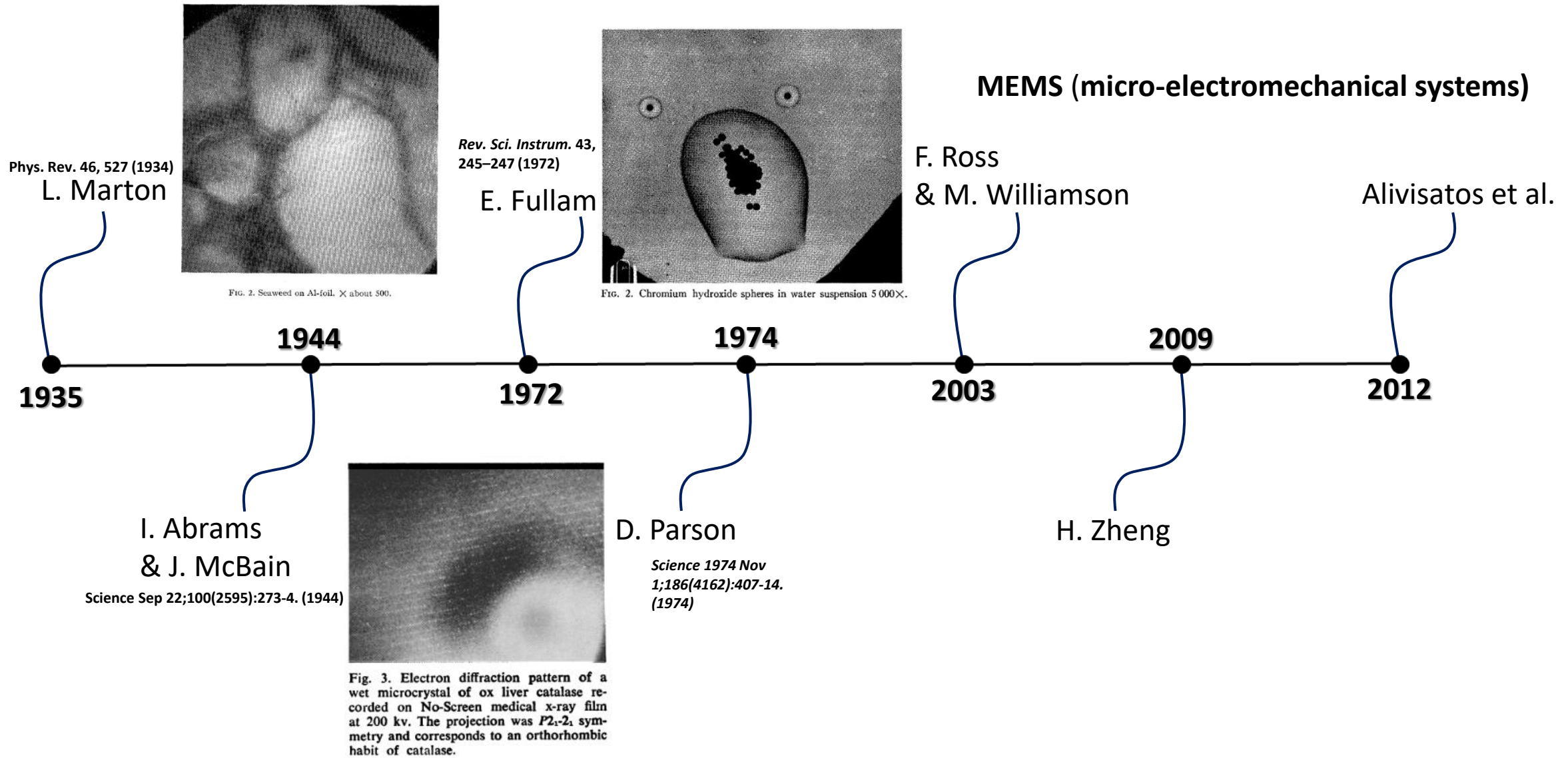


- No specific sample holder
- Easy sample preparation
- Restricted choice of liquid (no organic solvent, no water...)

- Tricky sample preparation
- Specific TEM sample holder
- Wide liquid choice
- possibility of liquid flow

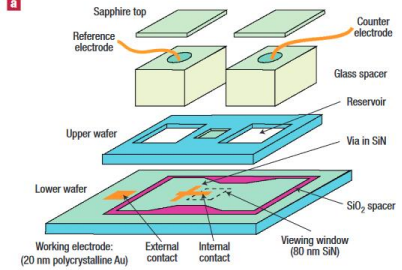
Pu, Shengda et al. "Liquid cell transmission electron microscopy and its applications." *Royal Society open science* vol. 7,1 191204. (2020) doi:10.1098/rsos.191204

MEMS (micro-electromechanical systems)



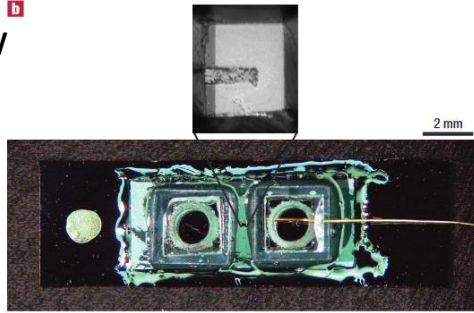
Sandwich-like design

SiN_x electron transparent window



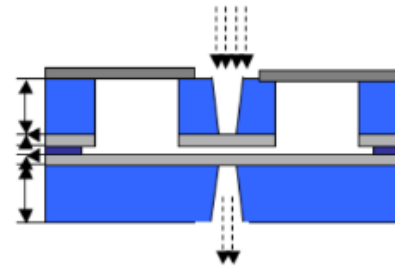
Nature materials
 vol. 2,8 (2003):
 532-6.

F. Ross et al.



Similar design

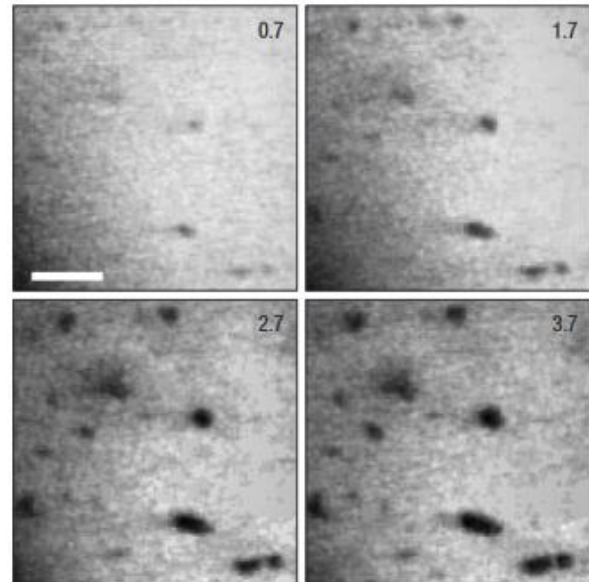
Cover
 Si: 100 μm
 SiN_x: 20 nm
 100nmSpacer
 SiN_x: 20 nm
 Si: 100 μm



Science 336,61-64(2012).
 Alivisatos et al.

Spatial
 resolution~ 5nm

2003



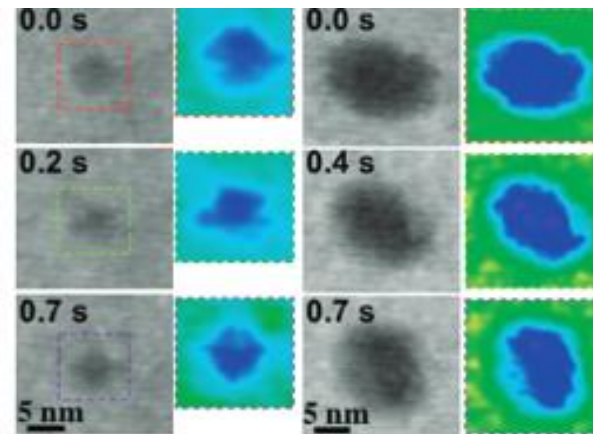
Cu
 cluster
 growth

2009

H. Zheng et al.
Nano Lett. 2009, 9, 6, 2460-2465

Diffusion
 during
 evaporation
 on Au NPs

Spatial
 resolution~ 1nm



2012

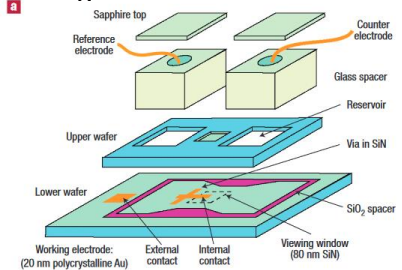


A Brief Historical of microchip liquid cell

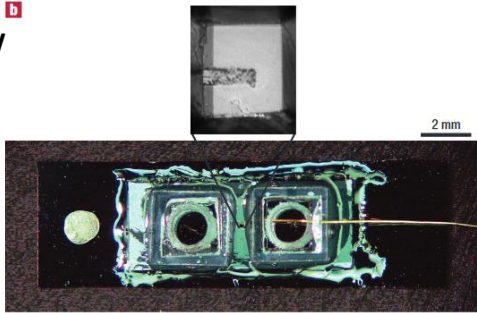


Sandwich-like design

SiN_x electron transparent window

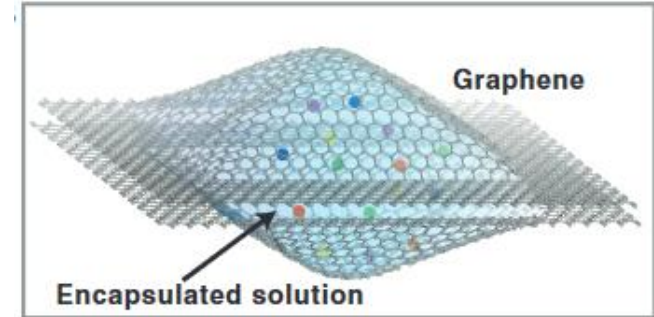
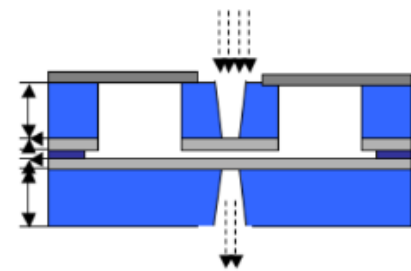


Nature materials
vol. 2,8 (2003):
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F. Ross et al.



Similar design

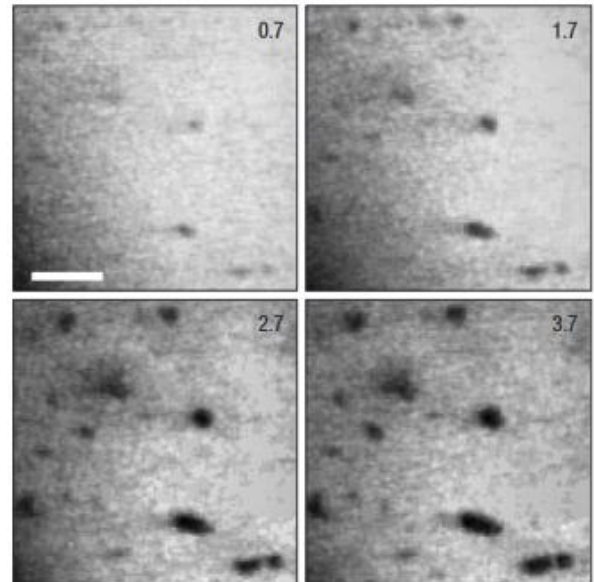
Cover
Si: 100 μm
SiN_x: 20 nm
100nmSpacer
SiN_x: 20 nm
Si: 100 μm



Science 336,61-64(2012).
Alivisatos et al.

Spatial resolution ~ 5nm

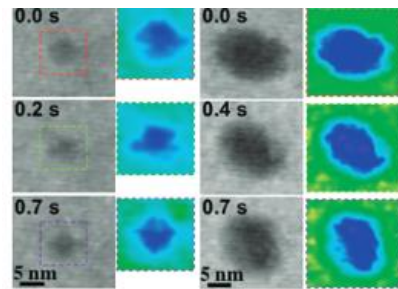
2003



Cu cluster growth

Spatial resolution ~ 1nm

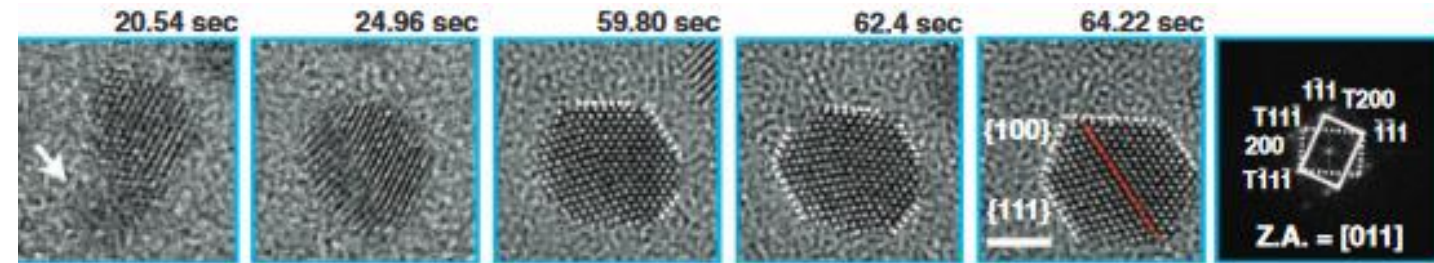
2009



H. Zheng et al.
Nano Lett. 2009, 9, 6, 2460-2465

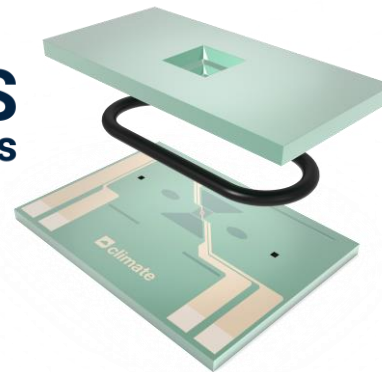
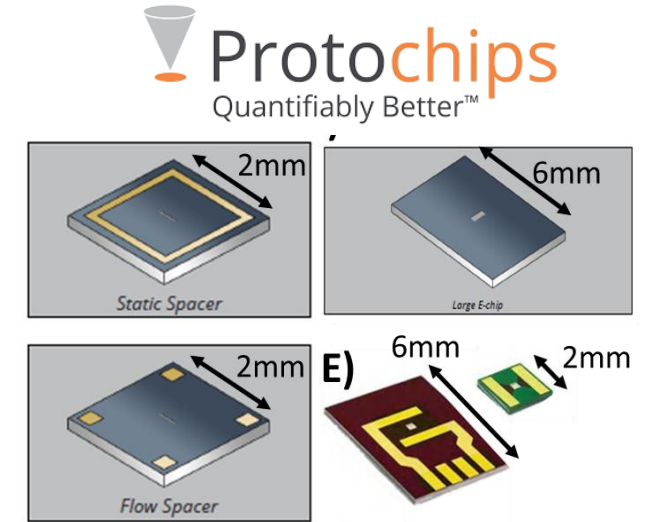
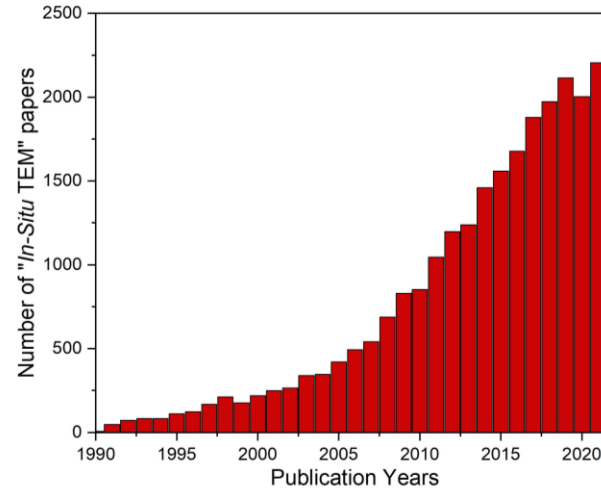
Diffusion during evaporation on Au NPs

Sub-nanometer (atomic) resolution



Colloidal Platinum growth

➔ A tremendous growing interest...

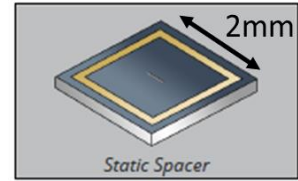
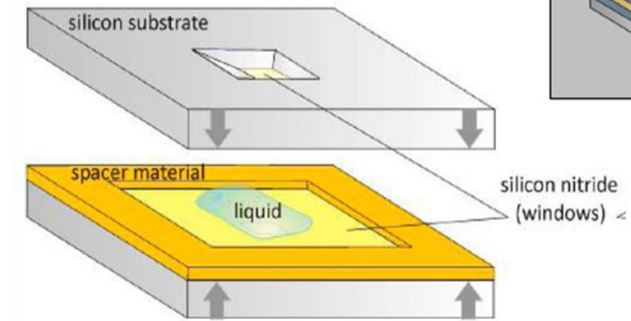


➔ ...which lead to many commercial solutions

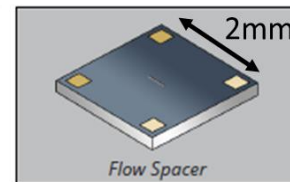
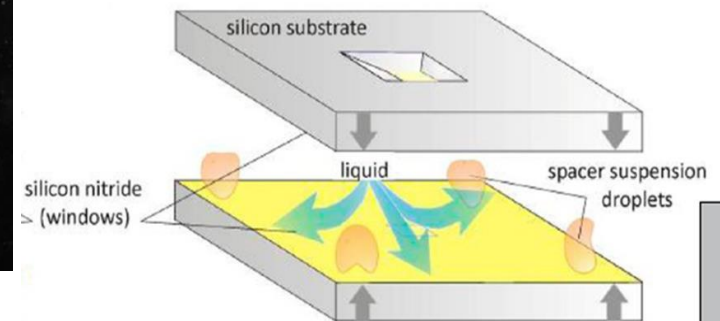


Two setup configurations:

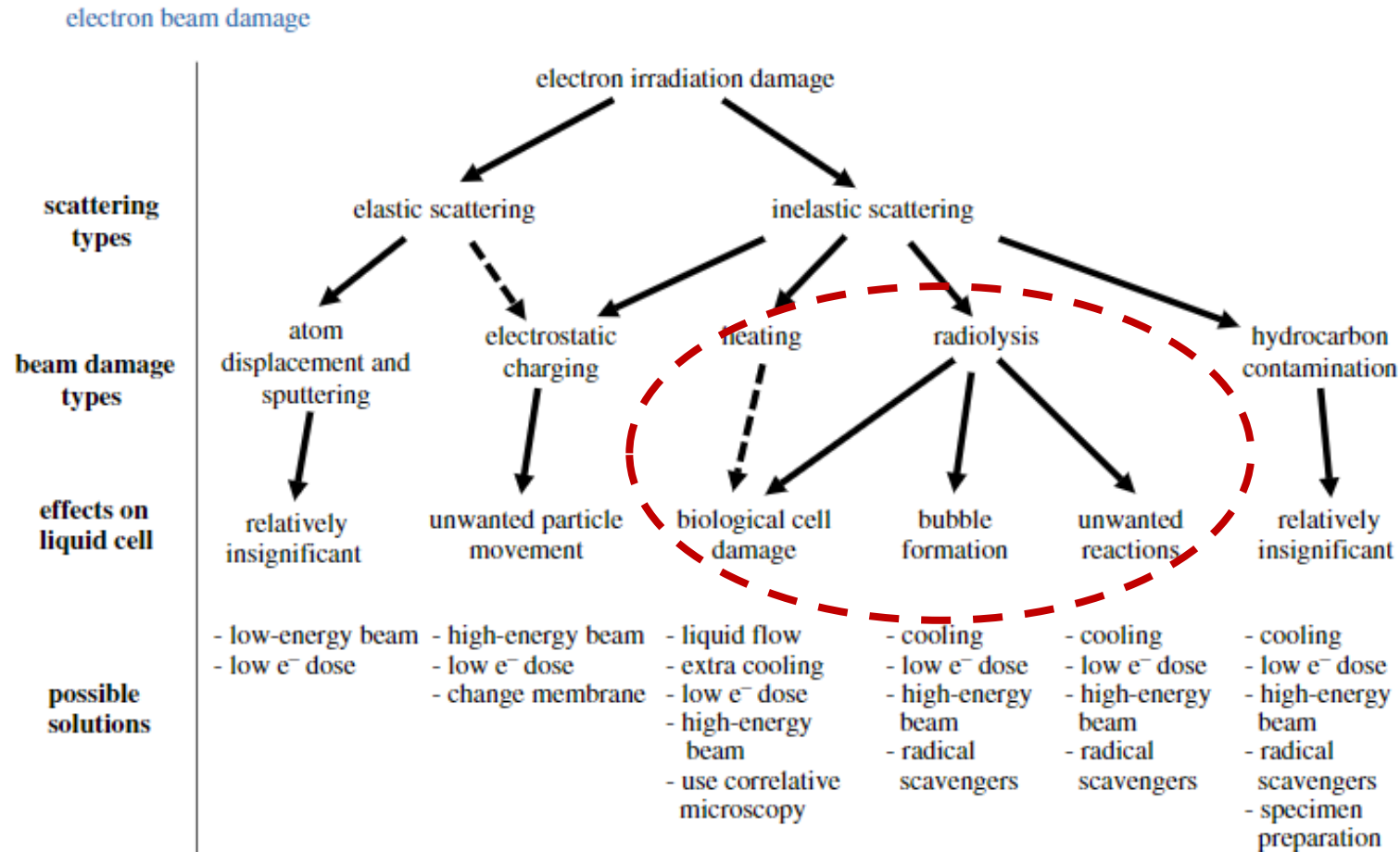
➔ Static cell



➔ Flow cell

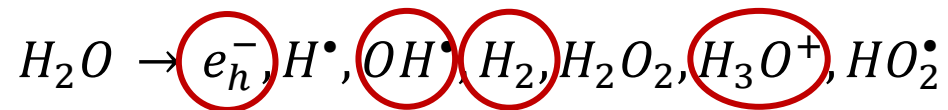


➔ Electron dose rate (radiation) : calculated in $e^- \cdot \text{\AA}^2 \cdot s^{-1}$

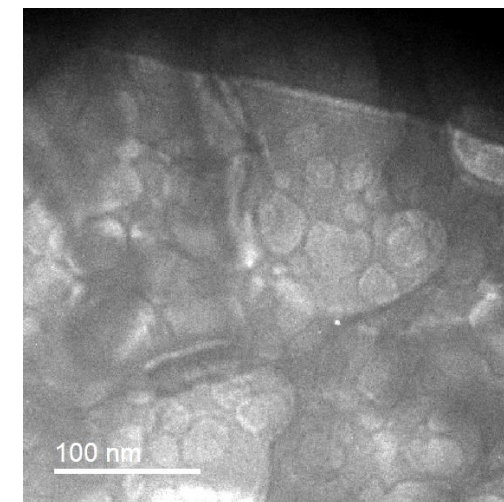
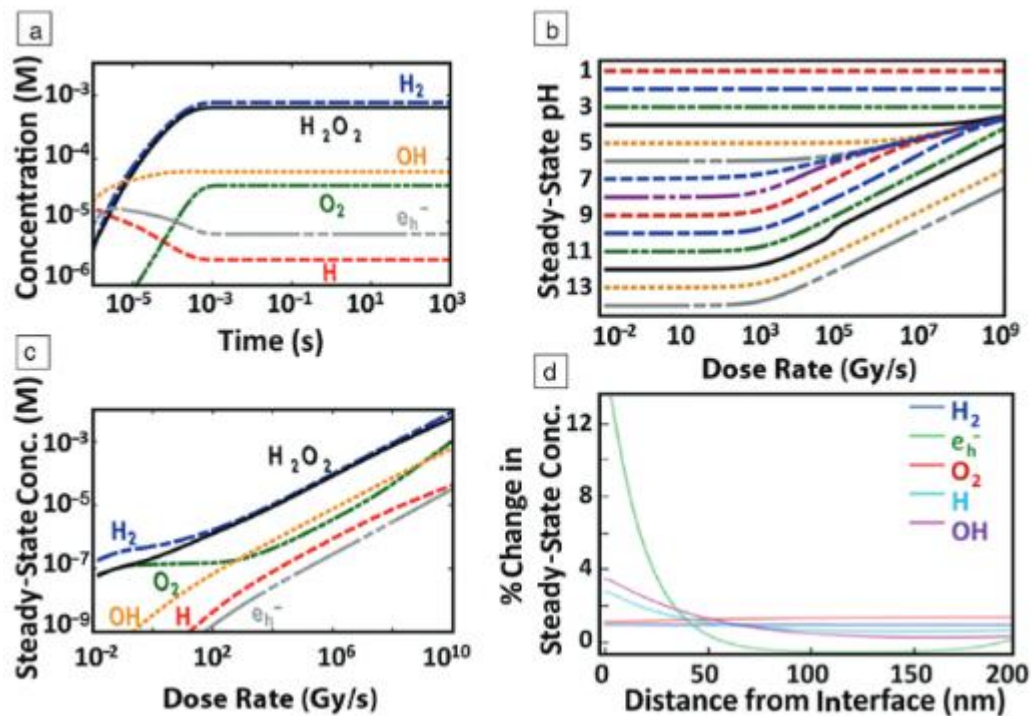


Pu, Shengda et al. "Liquid cell transmission electron microscopy and its applications." *Royal Society open science* vol. 7,1 191204. (2020) doi:10.1098/rsos.191204

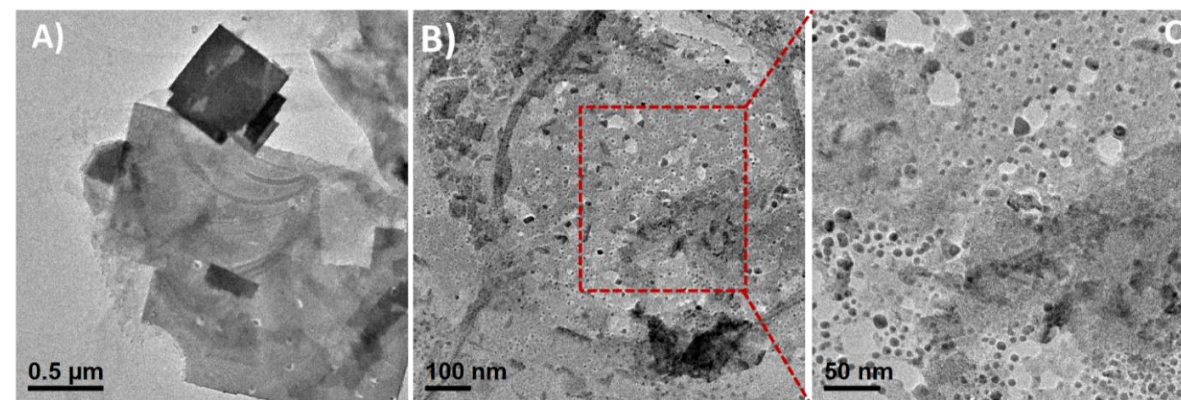
➔ Radiolysis of water



➔ Formation of H₂ bubbles

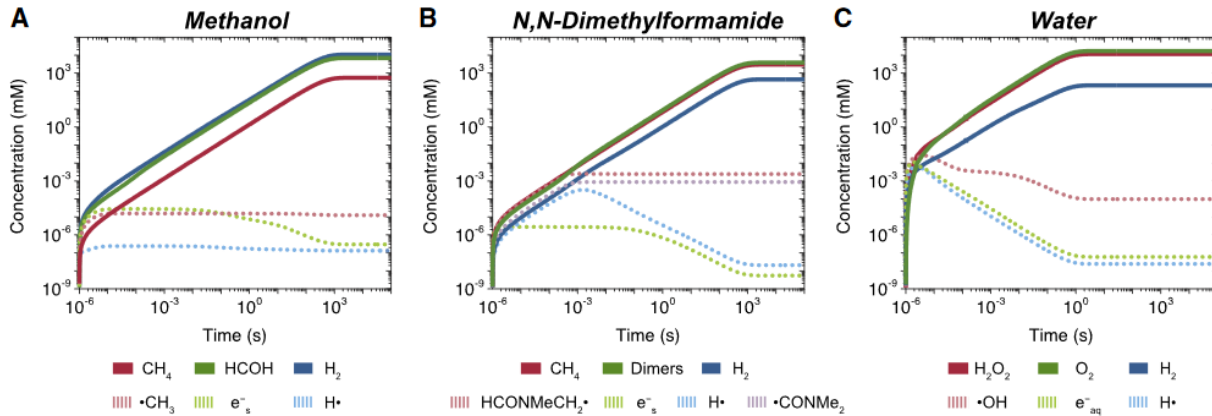


➔ Reduction of metal (Pb^{II} => Pb⁰)

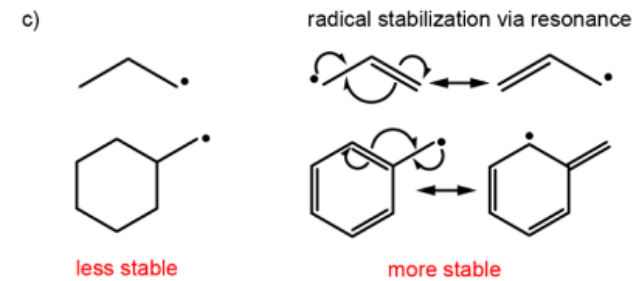
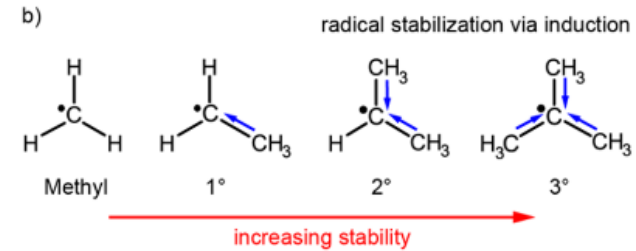


[MRS Bulletin](#), Volume 45, Issue 9: Liquid Phase Electron Microscopy, September 2020, pp. 746 - 753

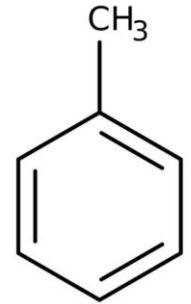
Radiolysis of organic solvent



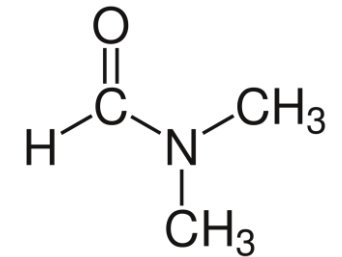
Cell Reports Physical Science, Volume 3, Issue 3, 16 March 2022, 100772



ACS Energy Lett. 2018, 3, 6, 1269–1278

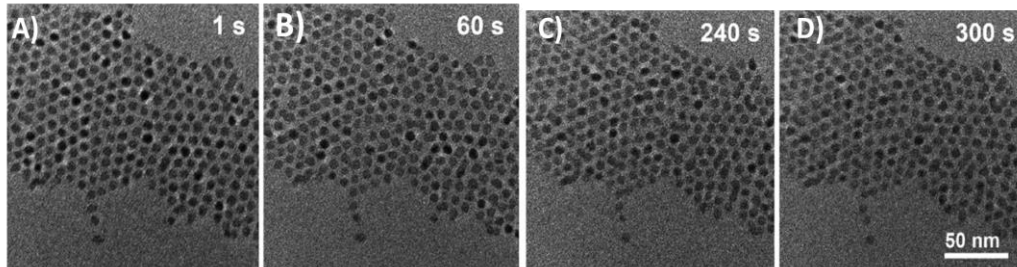


Toluene

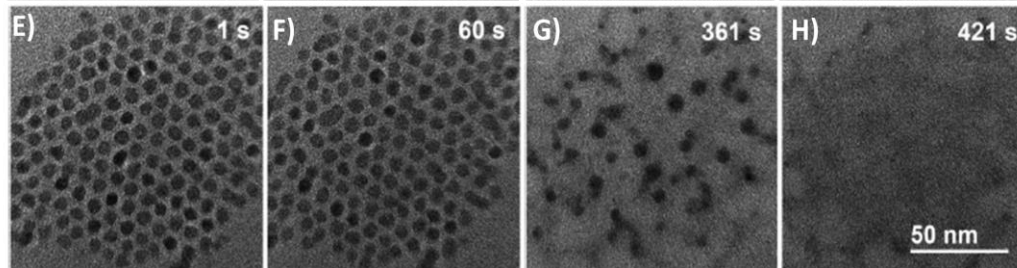


DMF

Moderate e^- dose
($50 e^- \cdot \text{\AA}^2 \cdot s^{-1}$)



High e^- dose
($200 e^- \cdot \text{\AA}^2 \cdot s^{-1}$)

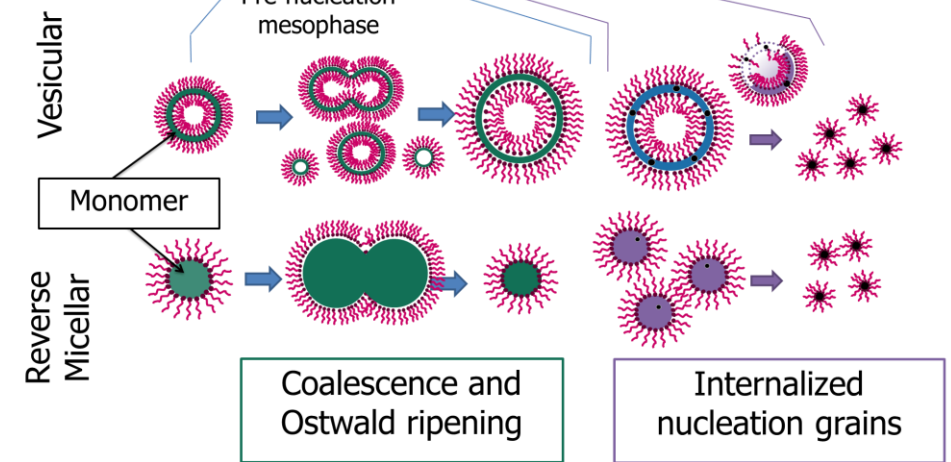
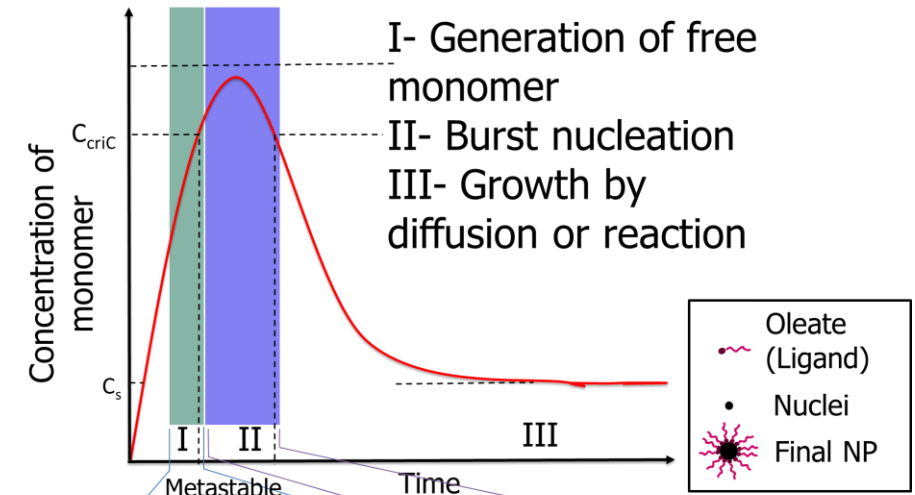
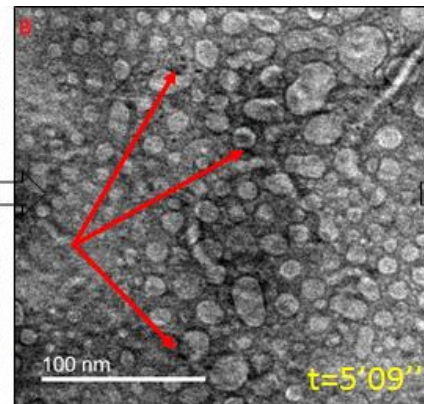
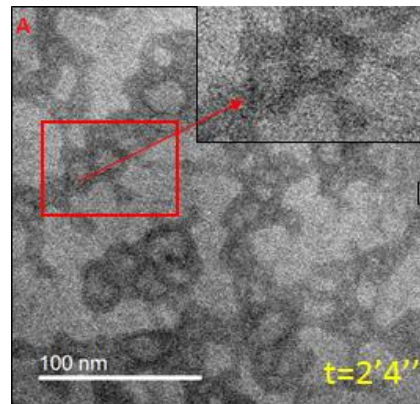
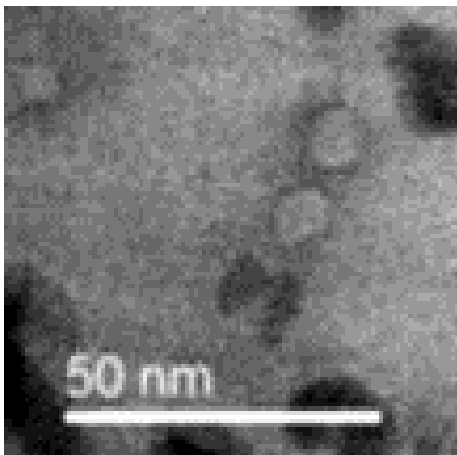
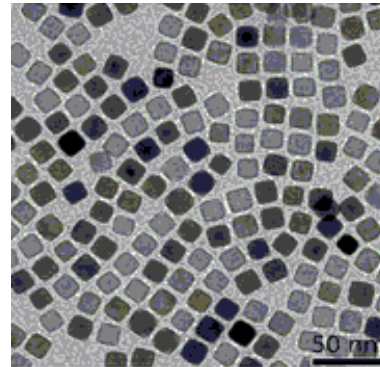
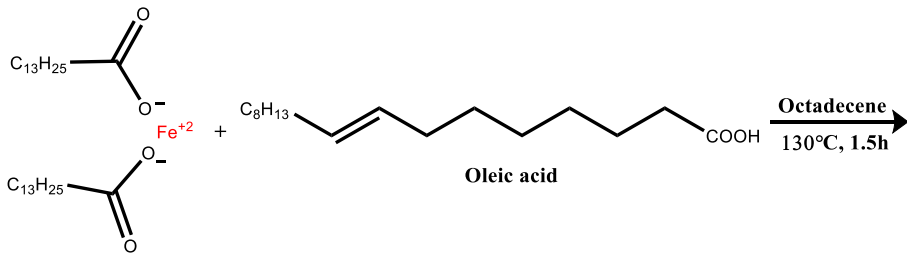


OH^- oxidizing PbTe
NPs and induced
etching

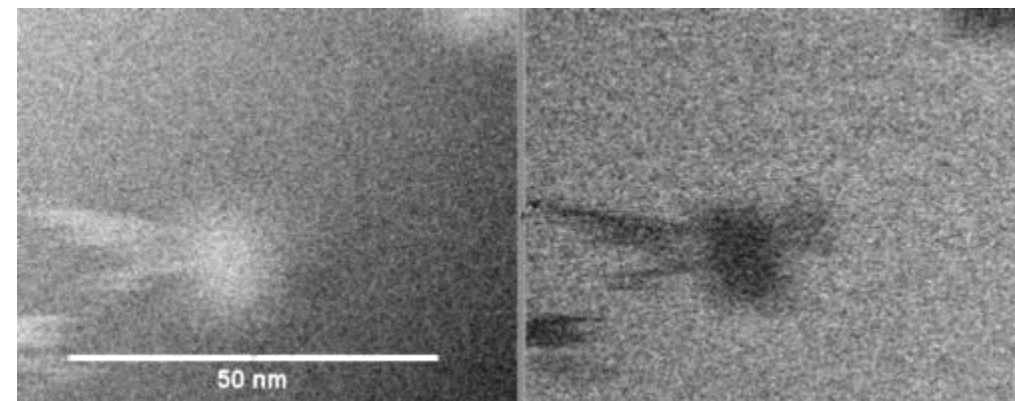
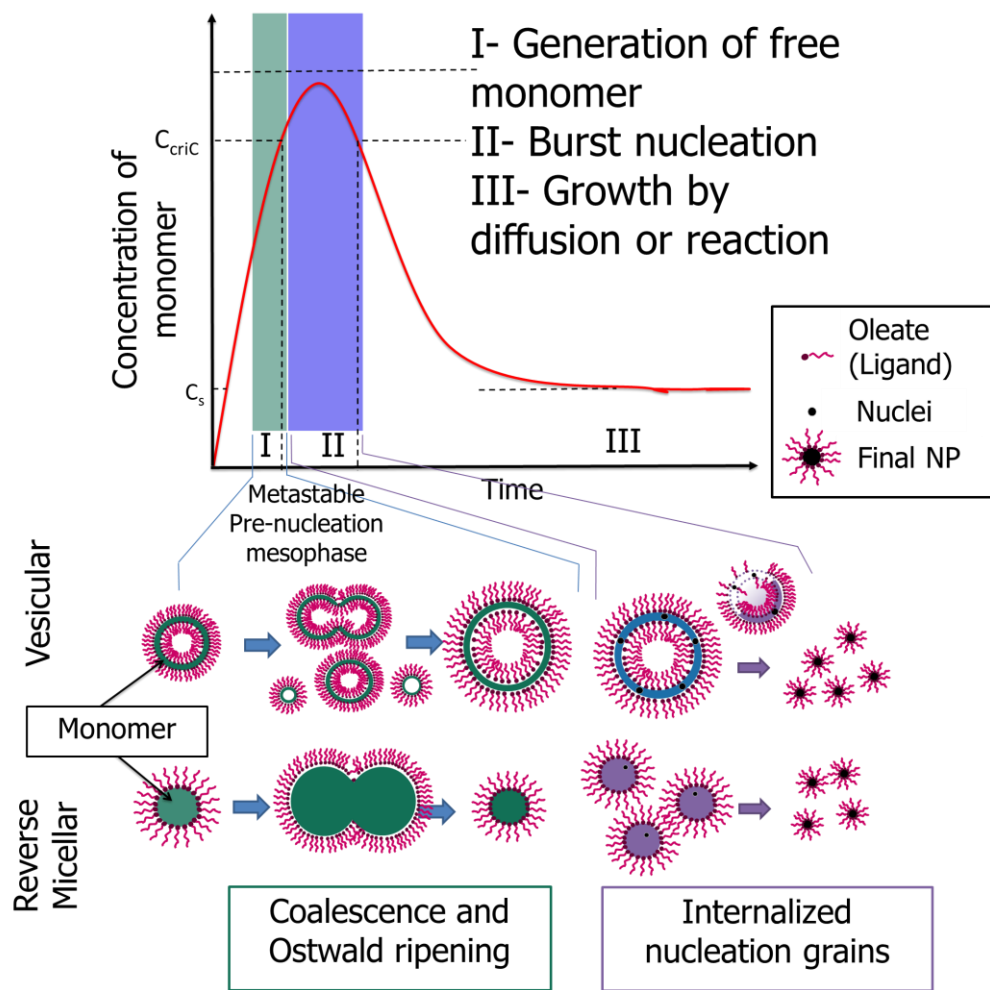
Be careful with the Water !

➔ Electron beam assisted reaction

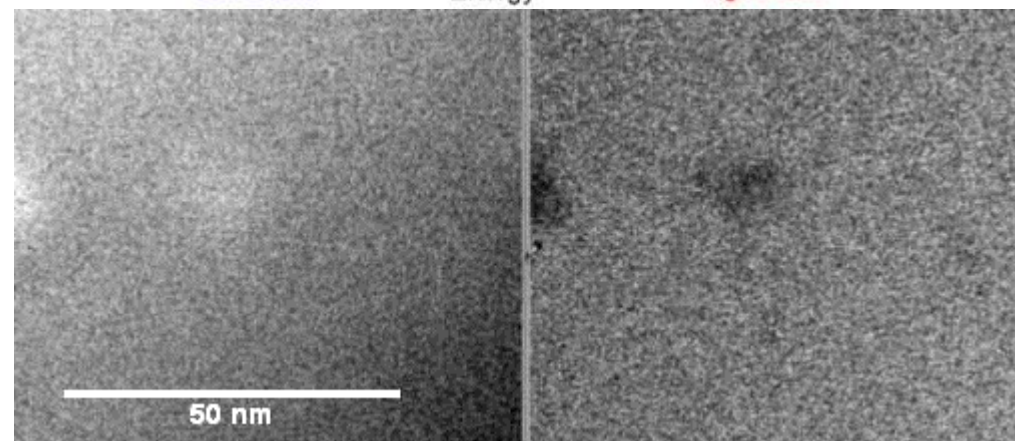
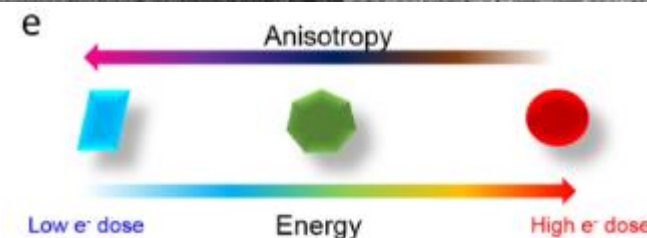
Nucleation and growth of Fe-based NPs by thermal decomposition



➔ Electron beam assisted reaction



Low e^- dose
 ($230 e^- \cdot \text{\AA}^2 \cdot s^{-1}$)



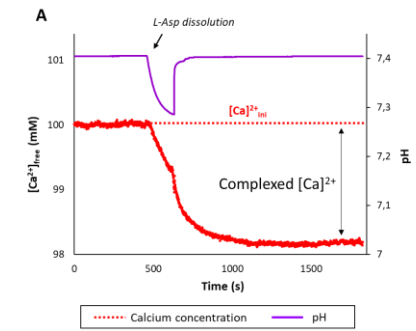
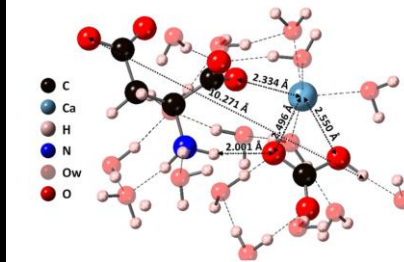
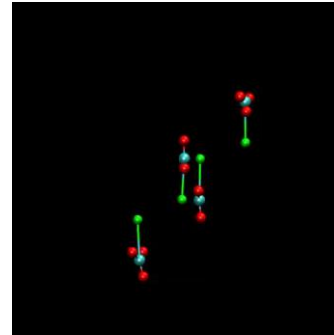
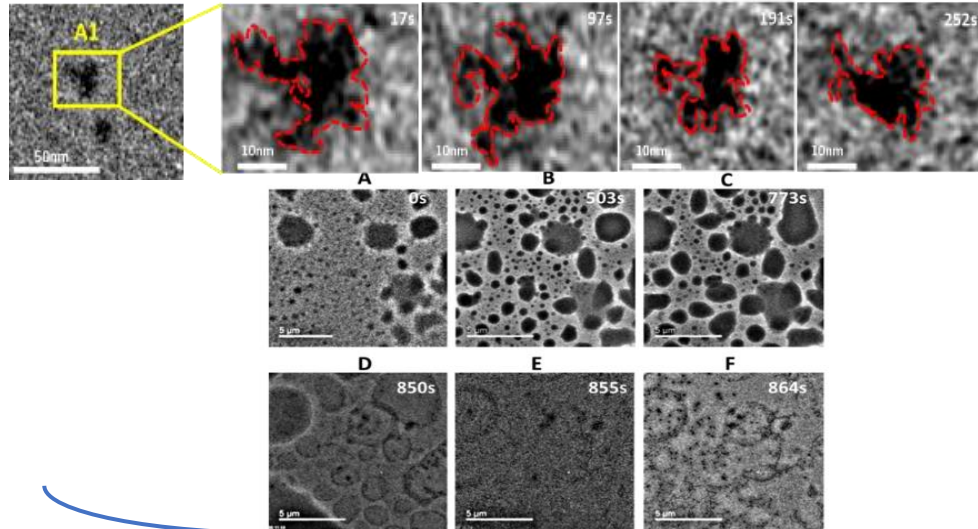
High e^- dose
 ($900 e^- \cdot \text{\AA}^2 \cdot s^{-1}$)

Nucleation and growth CaCO_3 : influence of L-aspartic acid

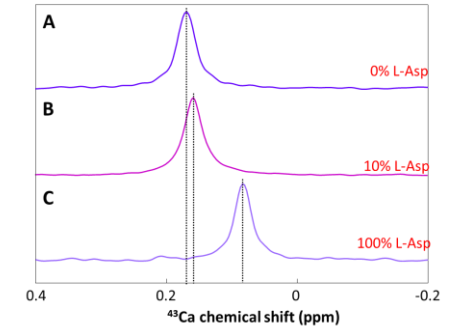
In-situ TEM

Simulation

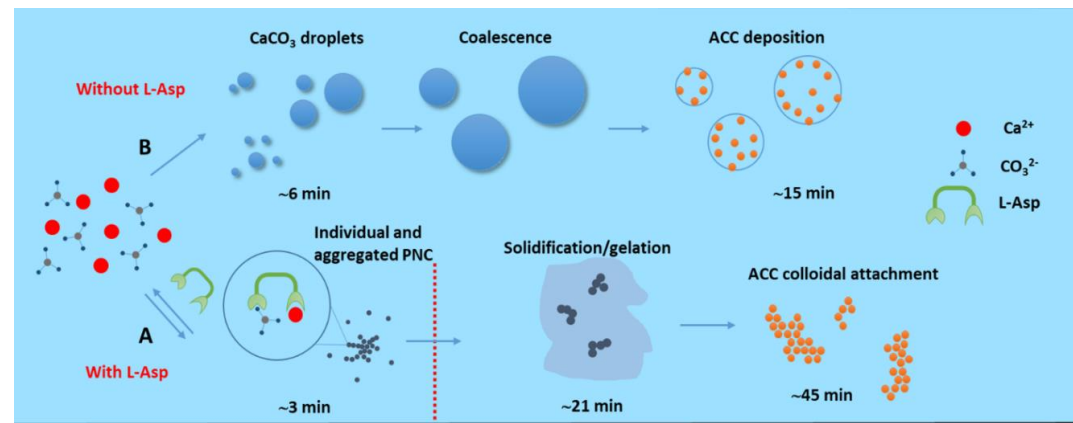
RMN



C



J. Am. Chem. Soc. 2022, 144, 33, 15236–15251

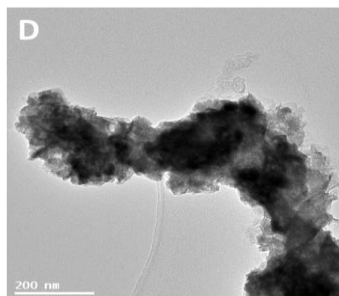
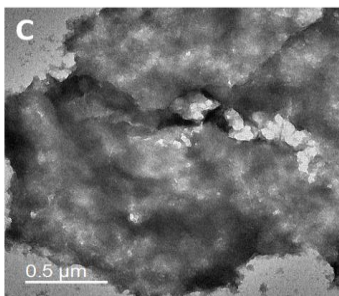
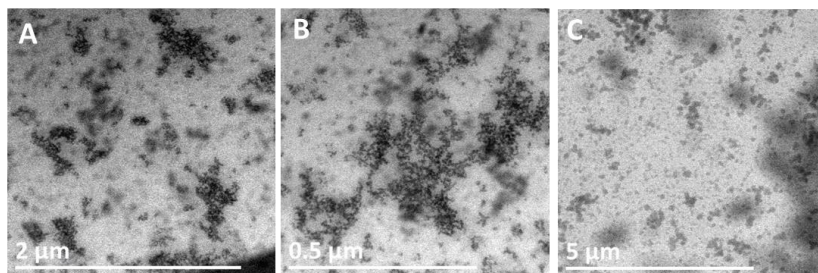
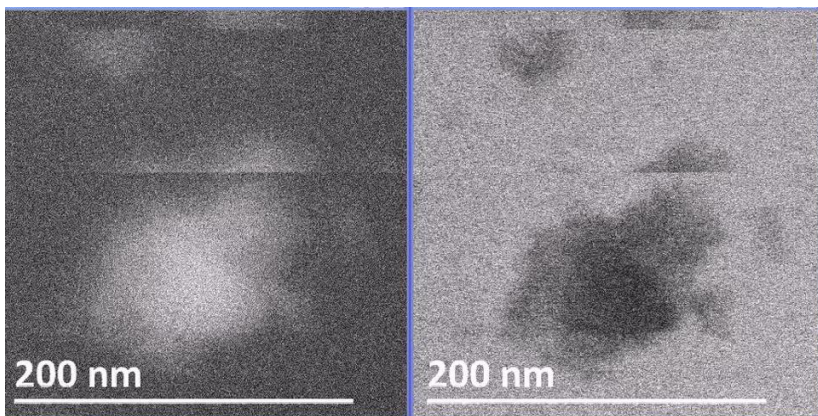


➔ Growth of tungsten oxide gel by « Chimie-Douce »

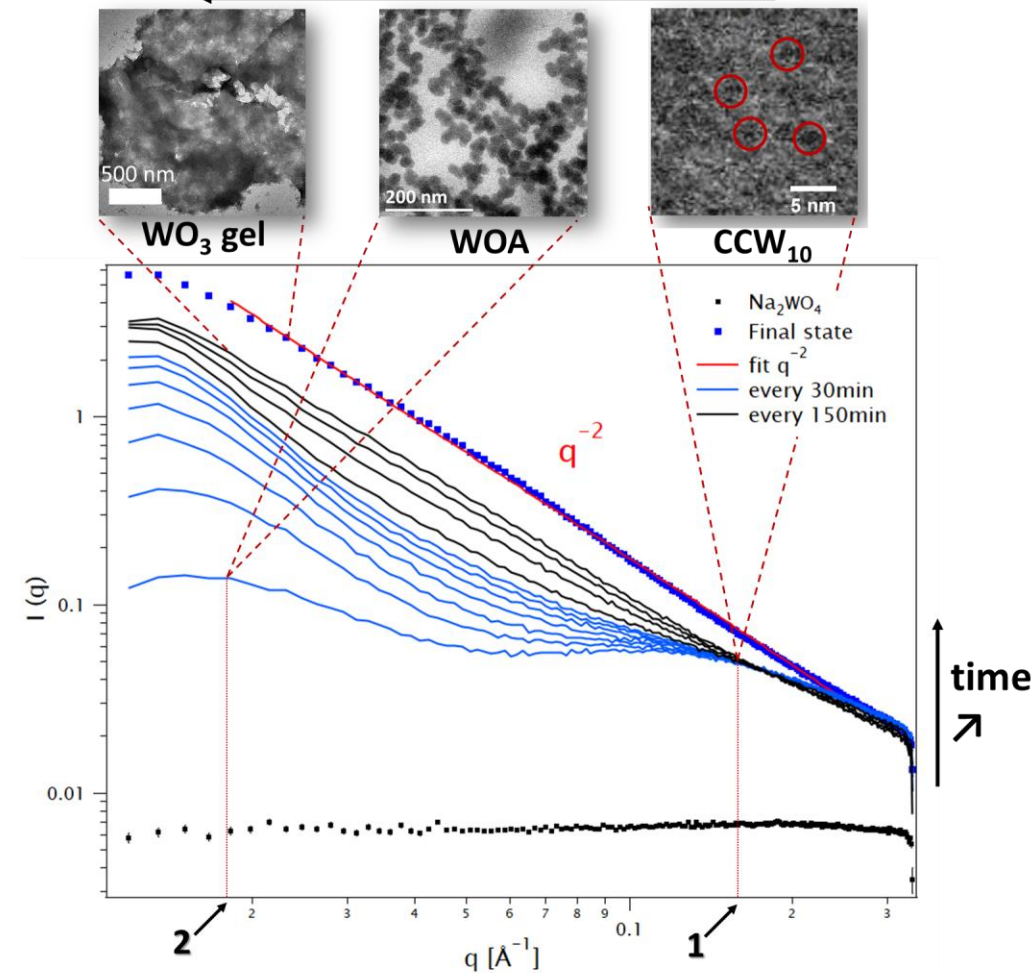
Combining local information with LPTEM...

...With average information with X-Rays Scattering

time



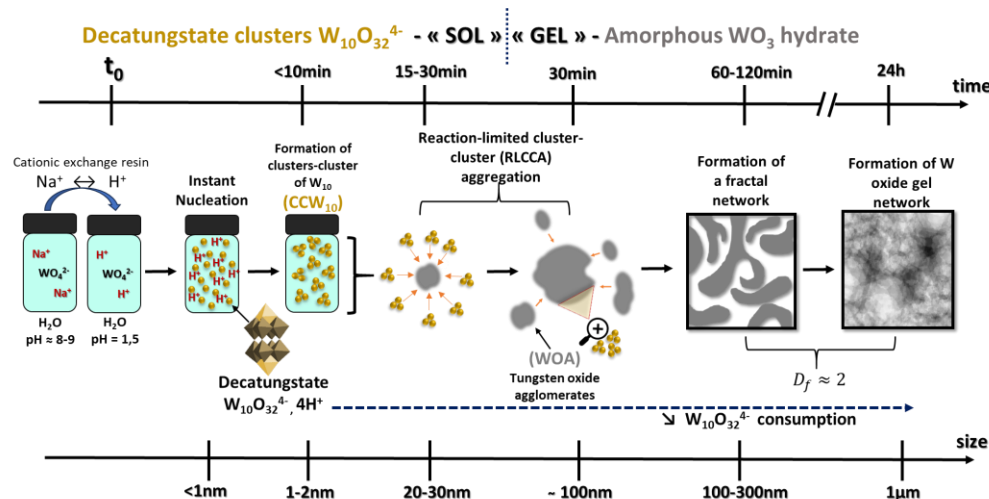
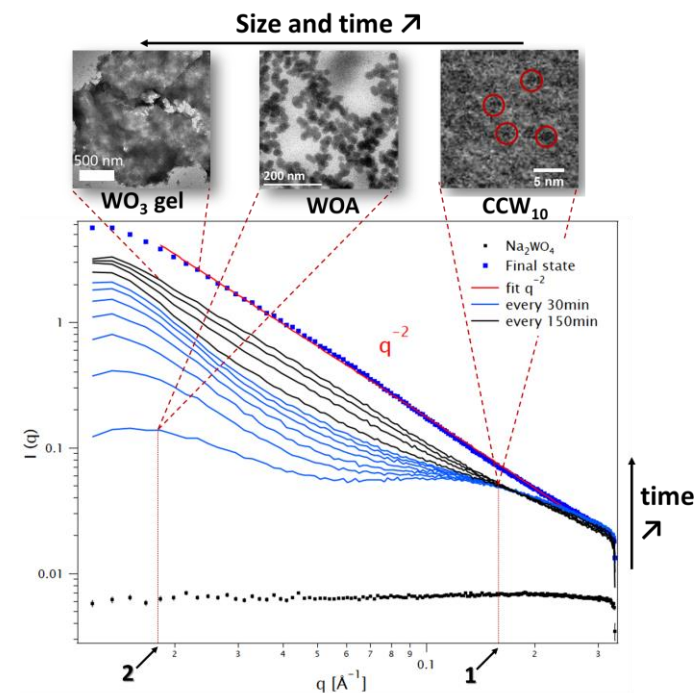
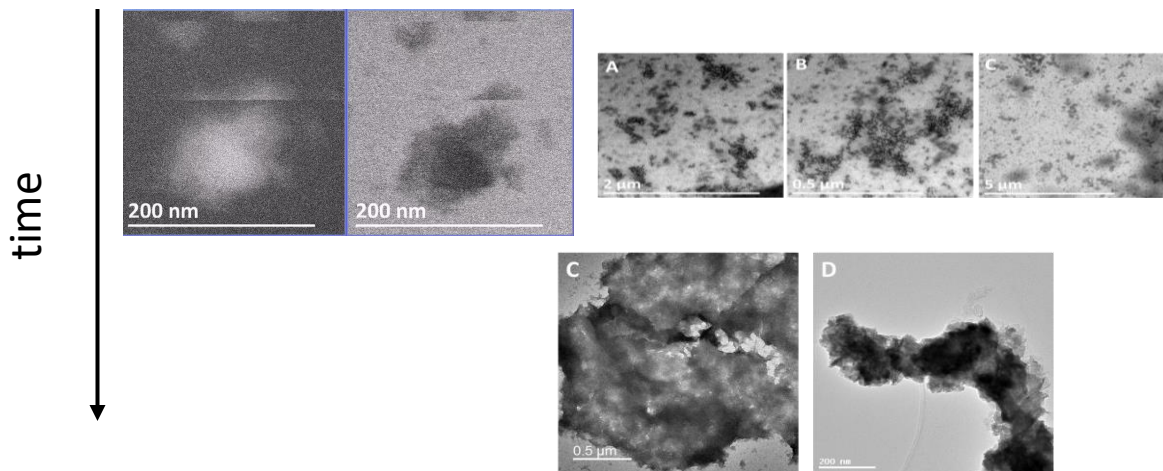
Size and time ↗



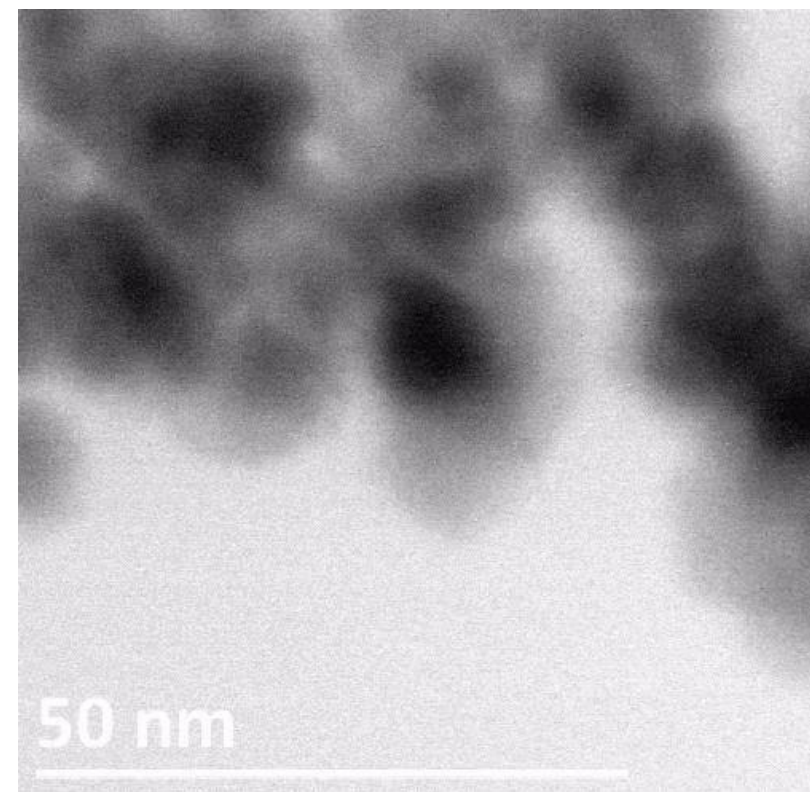
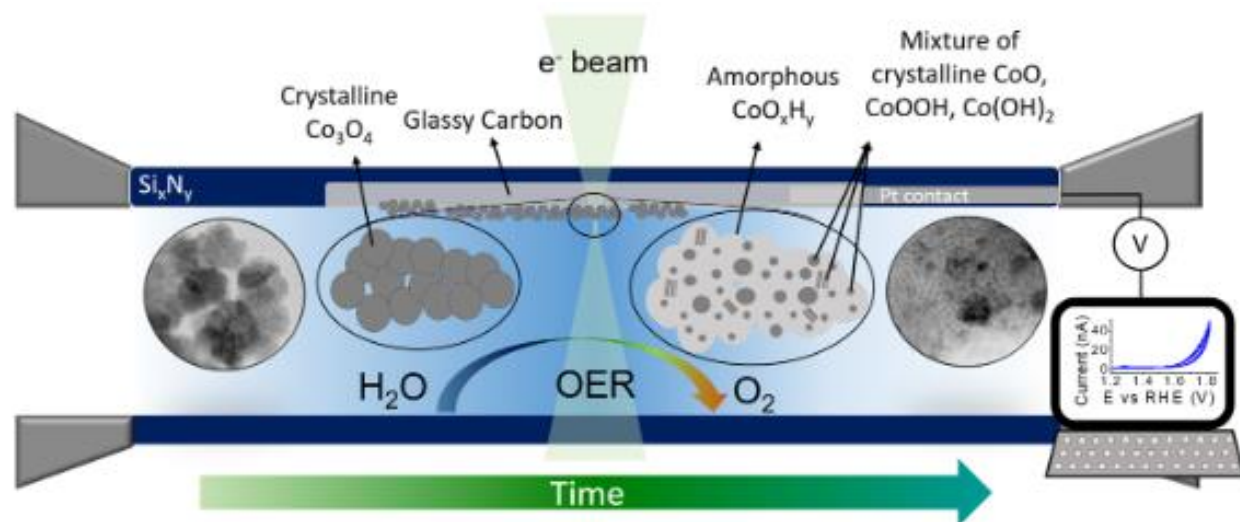
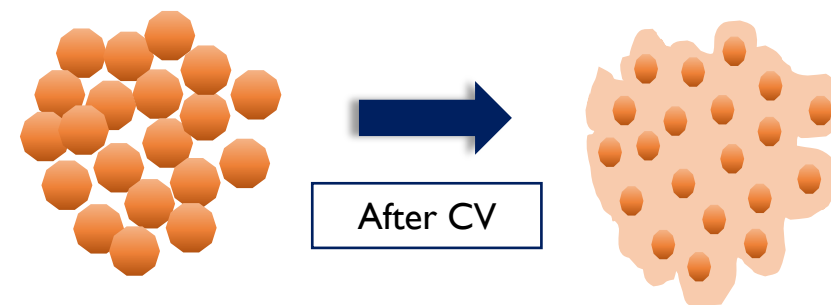
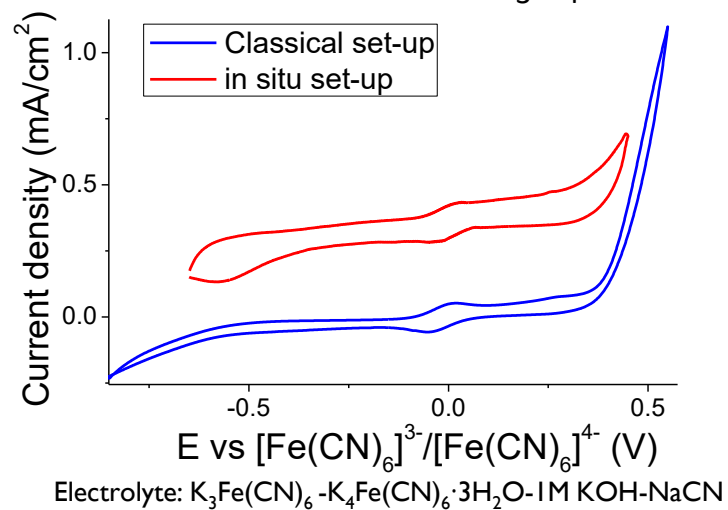
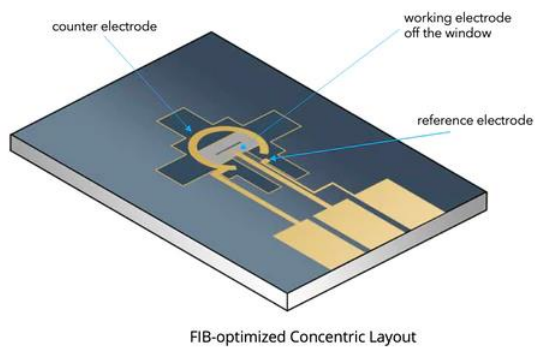
➔ Growth of tungsten oxide gel by « Chimie-Douce »

Combining local information with LPTM...

...With average information with X-Rays Scattering



Evolution of an electrocatalyst in *in-operando* conditions : Co_3O_4



ACS Nano 2019, 13, 11372-11381



- ➔ Development of closed cell for LPTEM enable to image a wide range of liquid with nanometer resolution

- ➔ Possibility to study many phenomena :
 - Nucleation and growth of nanomaterials
 - Biological phenomena
 - Electrochemistry
 - Self-assembly, nanoparticles movement, battery....

- ➔ Always take in account liquid radiolysis, especially with water!

- ➔ **Try to always performed complementary techniques and correlate them with your TEM observations.**