Université de Strasbourg

Microscopie électronique en temps réel et corrélative pour l'étude de la matière : naissance, vie et transformation des nanomatériaux

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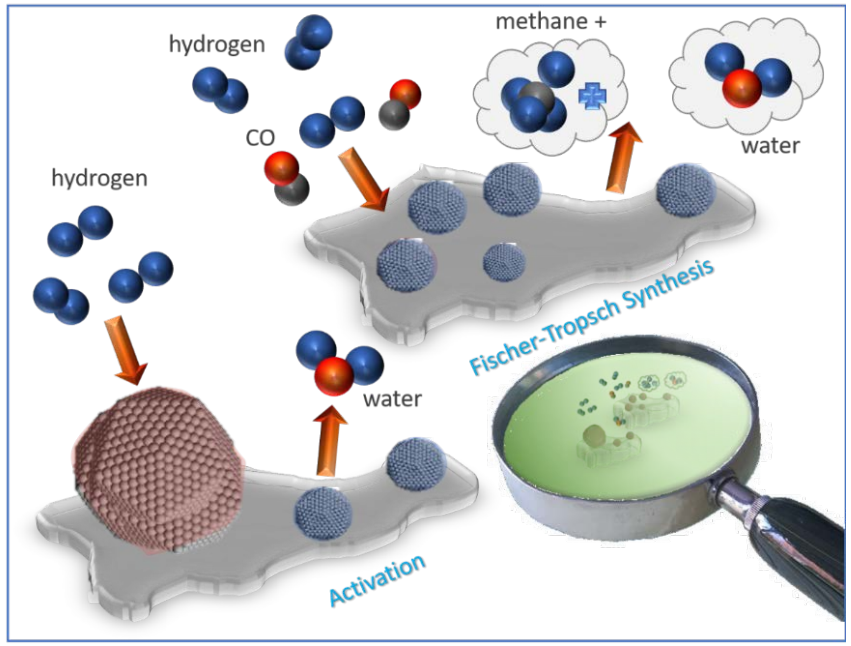
Nivedita SUDHEER, Valentina GIRELLI, Sharmin SHARNA, Sivagen VYDELINGUM
Virgile ROUCHON, Maxime MOREAUD, *autres collaborateurs @ IFPEN, @PHENIX, @CRMN*



IPCMS Institut de Physique et Chimie des Matériaux de Strasbourg

3D TEM TEAM

METSA

CARMEN Caractérisation des matériaux pour les énergies nouvelles
Laboratoire Commun de Recherche
CNRS
ENS de Lyon
IFP Energies nouvelles
Sorbonne Université
Université Claude Bernard Lyon 1
Université de Strasbourg

Porous materials & materials for new energies

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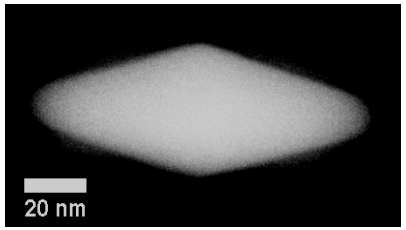
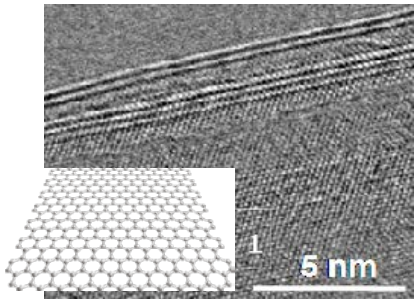
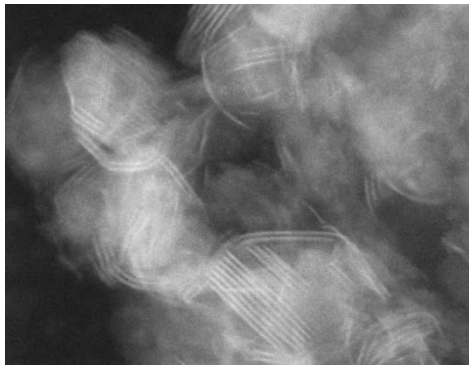
Nanoparticles, nanowires

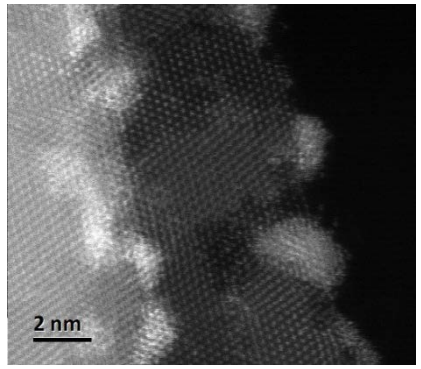


1-,2-,3-D Carbon nanostructures

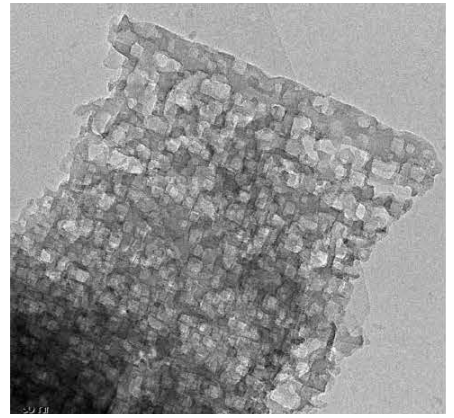


Nanomaterials for catalysis





Porous materials

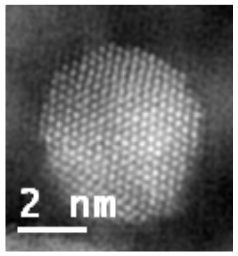


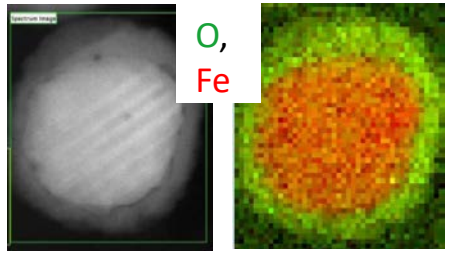
Properties of interest: *morphology, shape, 3D architecture, electronic and crystallographic structures…..*

In situ: *structural evolution, reactivity, phase transformation, restructuration, growth, synthesis …*

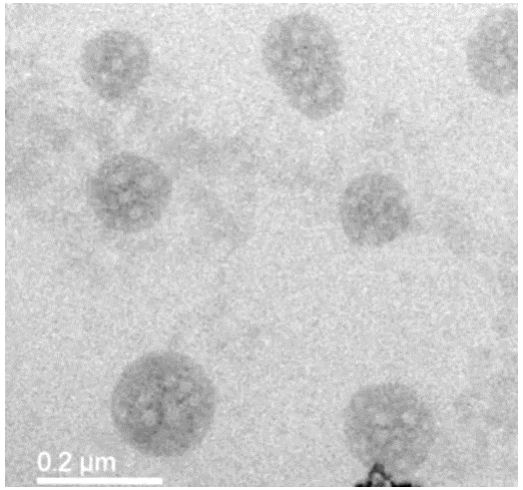
Why electron microscopy?

- **Resolution: µm → Å**
- **« Real space » images**
- **Very localized information**





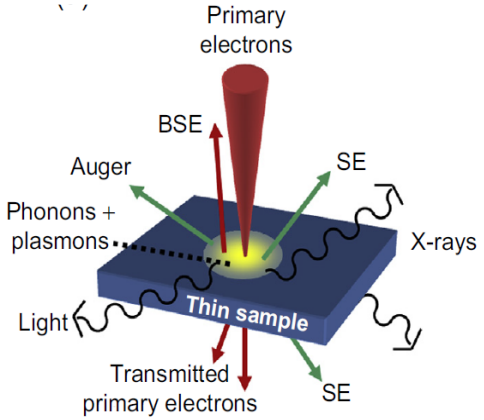
- **Possibility to combine with various "in-situ" approaches**



In situ TEM under temperature, electric potential and/or specific environment

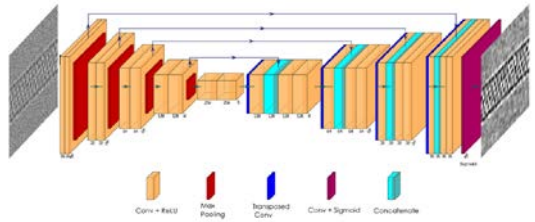
"Operando" TEM to mimic the "real" conditions

- **Strong interaction electron beam & specimen → various types of information**



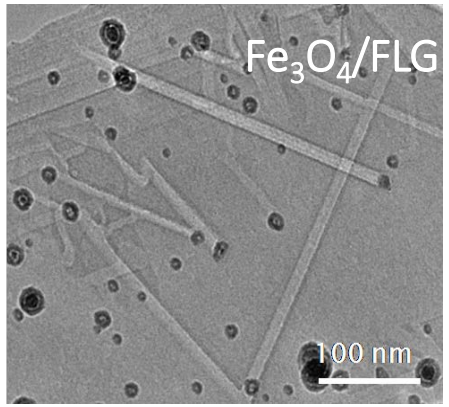
- **LARGE AMOUNT OF DATA**

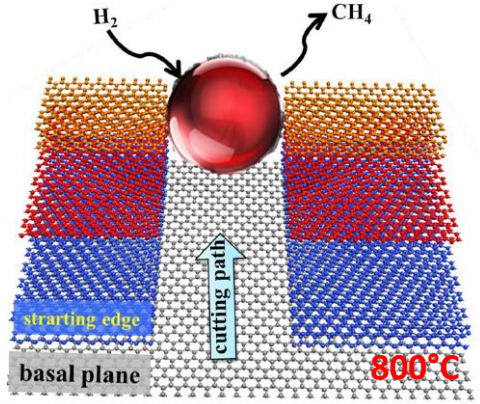
Machine Learning-based tools (ANR ARTEMIA)

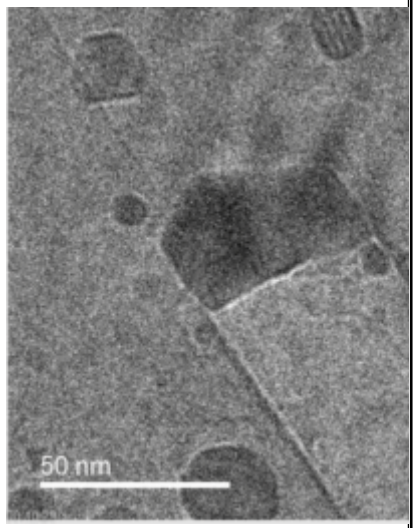


Examples of advanced TEM studies

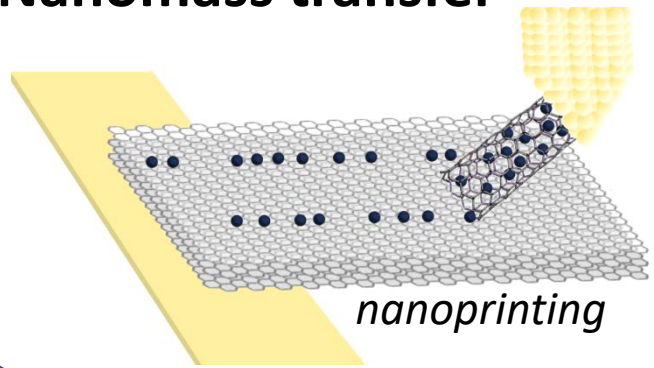
In situ nanostructuration process

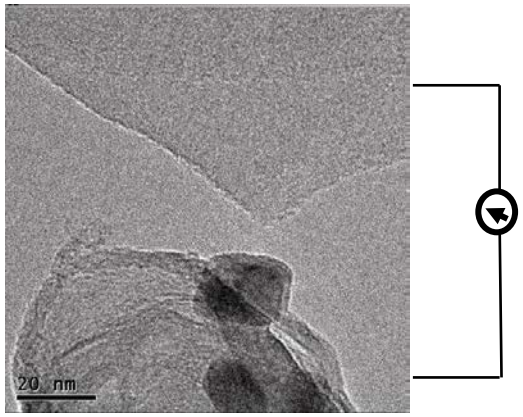




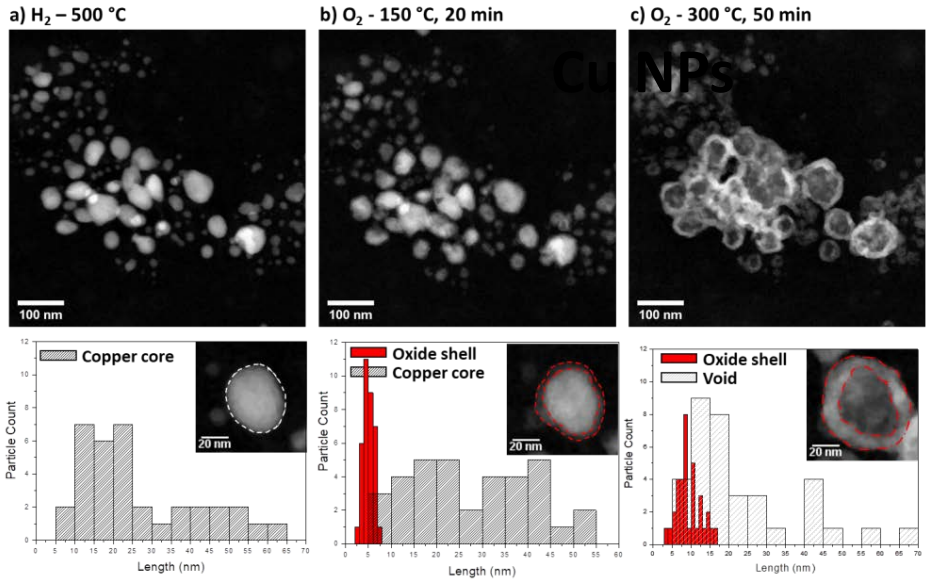


Nanomass transfer





Measure of physical properties

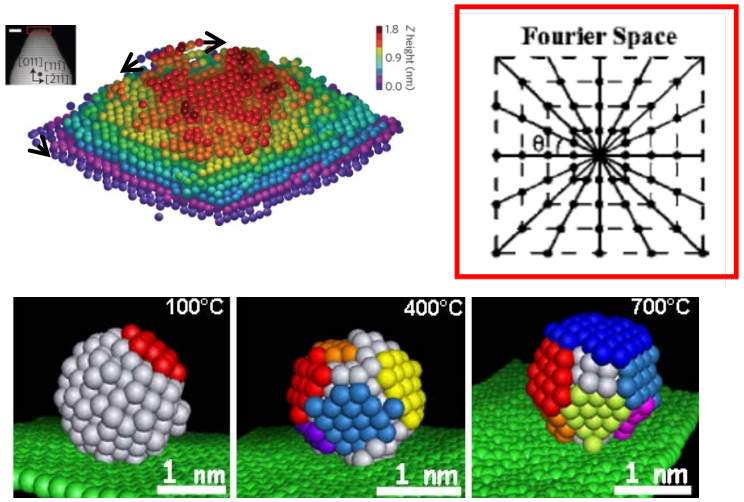


Diffusion coefficient (@150°C): 9.5×10^{-19}

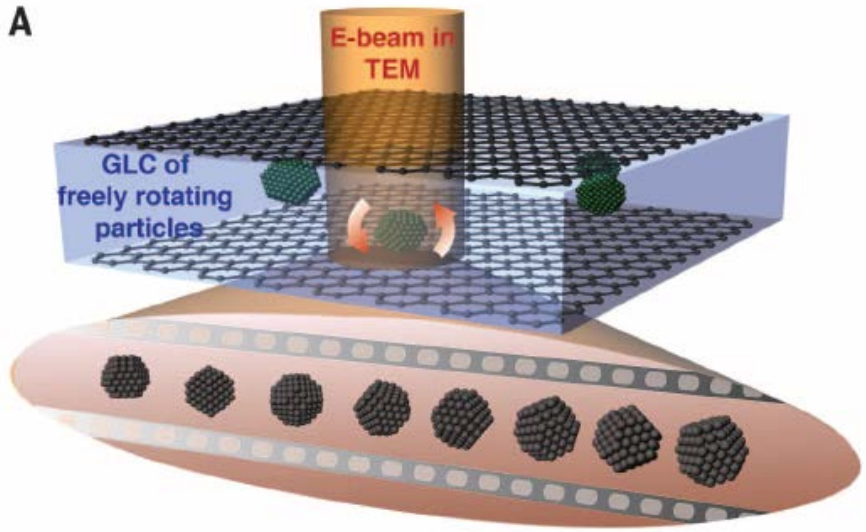
Activation energy : 31.4 kJ/mol

Examples of advanced TEM studies

3D atomic resolution

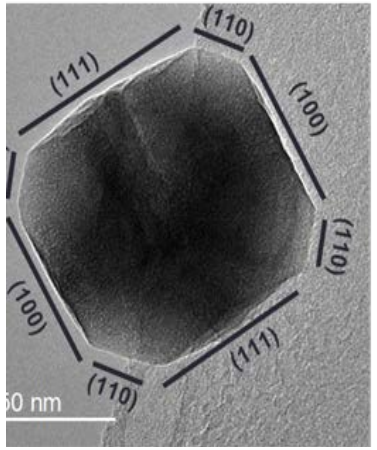


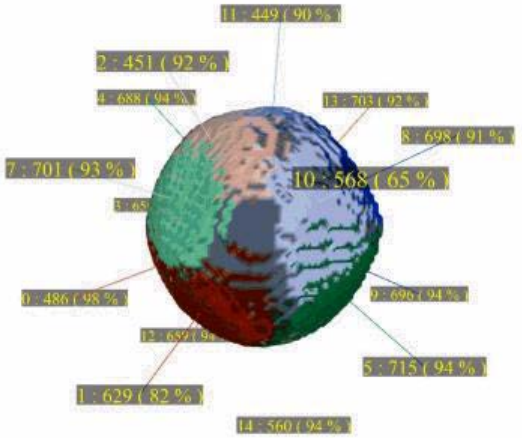
3D image from a free motion

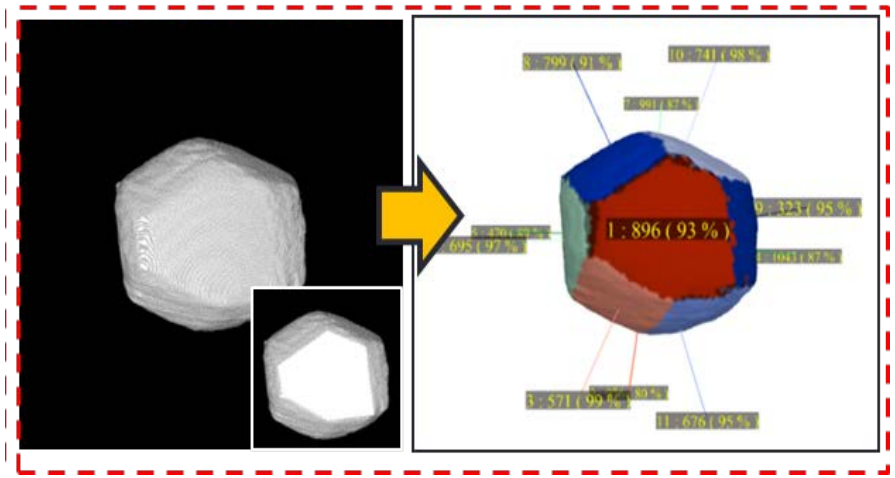


J. Park et al, Science 349, 6245, 2015

Data quantification







Electron microscopy in CARMEN

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Université de Strasbourg

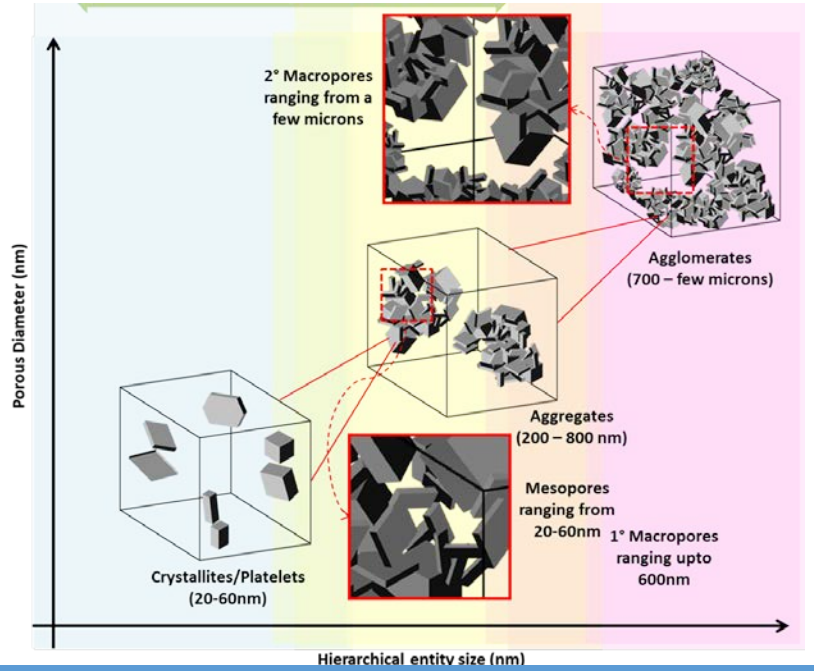

V. Girelli Consolaro


N. Sudheer

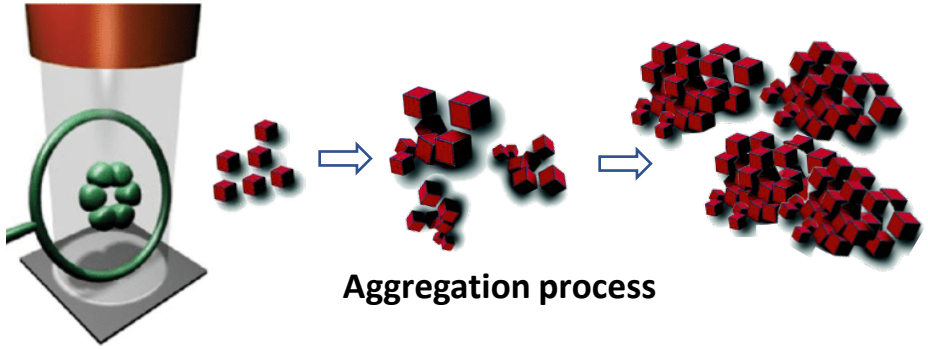

S. Vydelingum


S. A. Sharna

Multiscale analysis

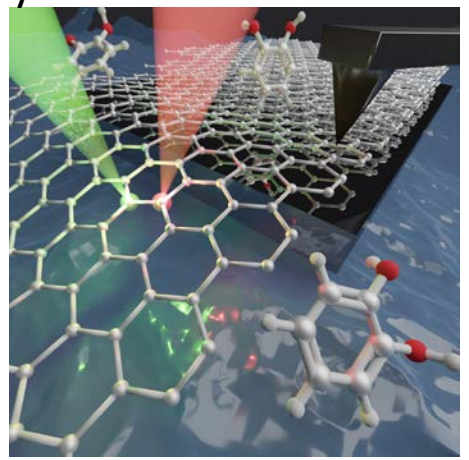


In situ, real time monitoring


Aggregation process

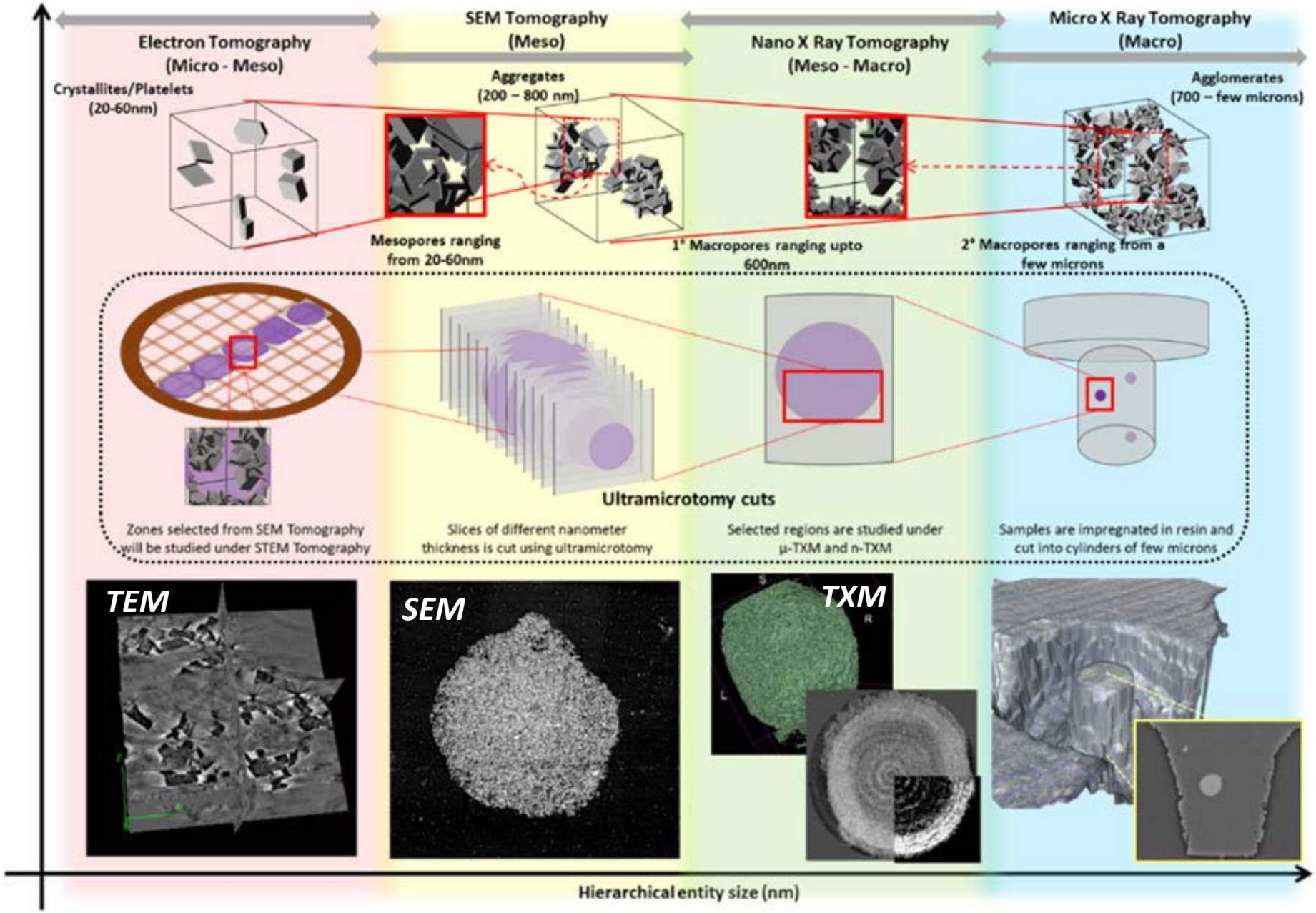
Correlative study

X-rays electrons AFM tip



Electron microscopy in CARMEN: mutiscale analysis

N. Sudheer



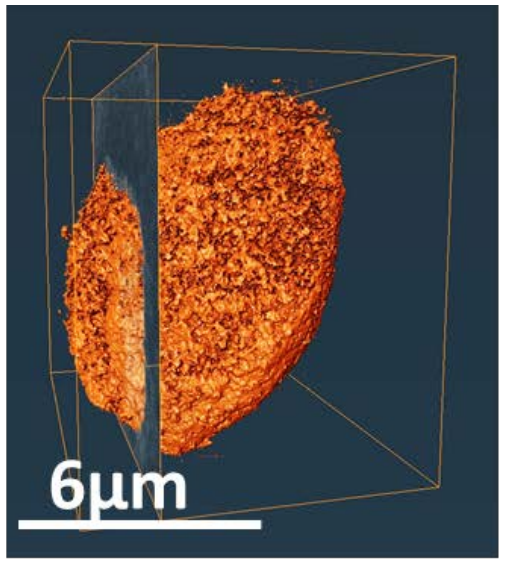
Electron microscopy in CARMEN: mutiscale analysis

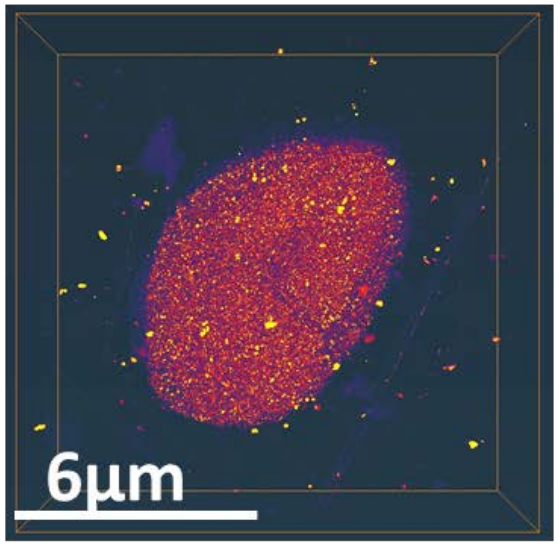
N. Sudheer

TXM Tomography

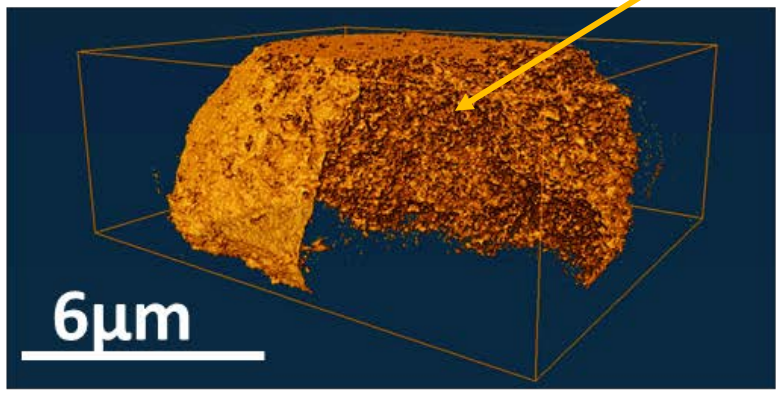
SEM Tomography

Pixel Size = 17nm

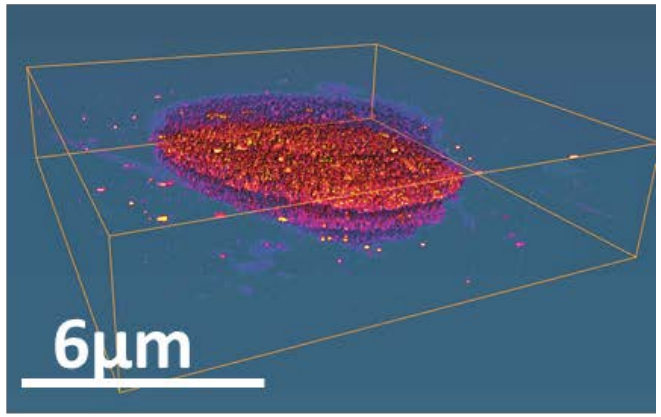




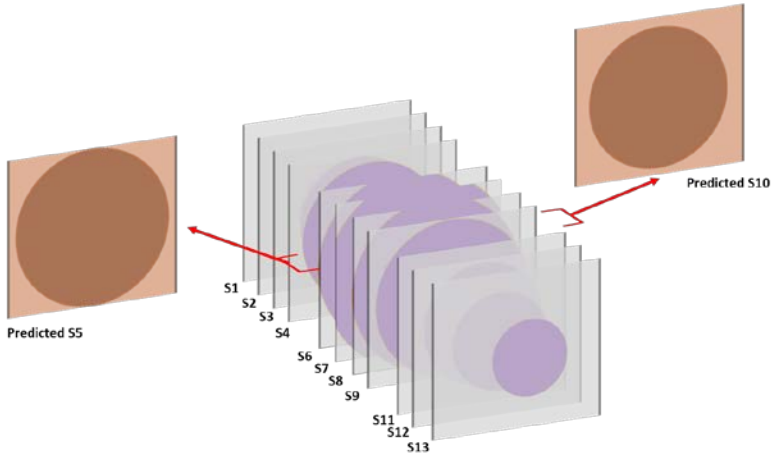
Observations of volume being hollow due to artifacts



Pixel Size = 4nm



FILLING THE PLOT HOLES : IMPLEMENT DEEP LEARNING

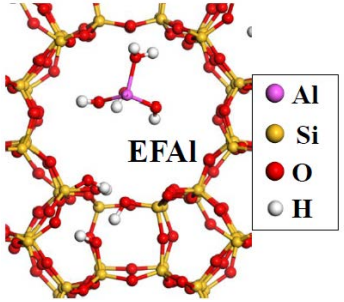


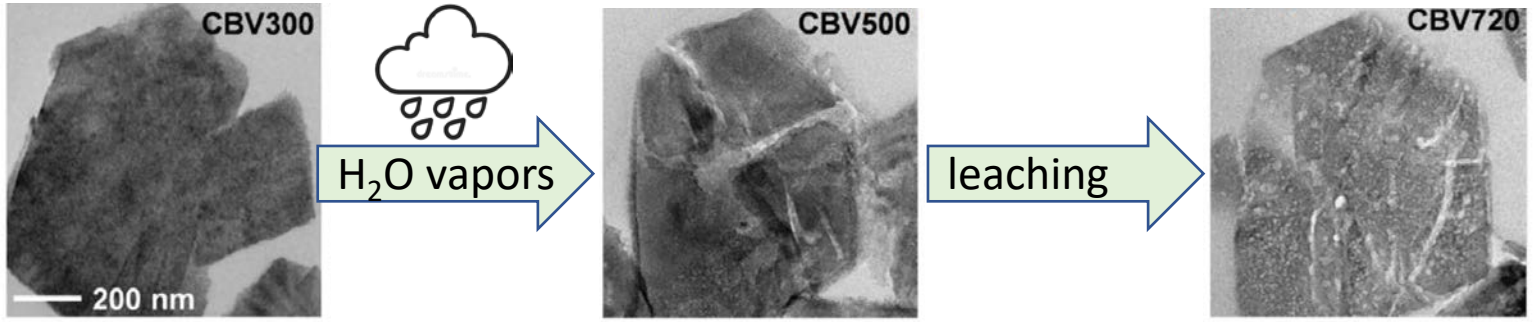
Super resolved n-TXM volumes

Electron microscopy in CARMEN: in situ study

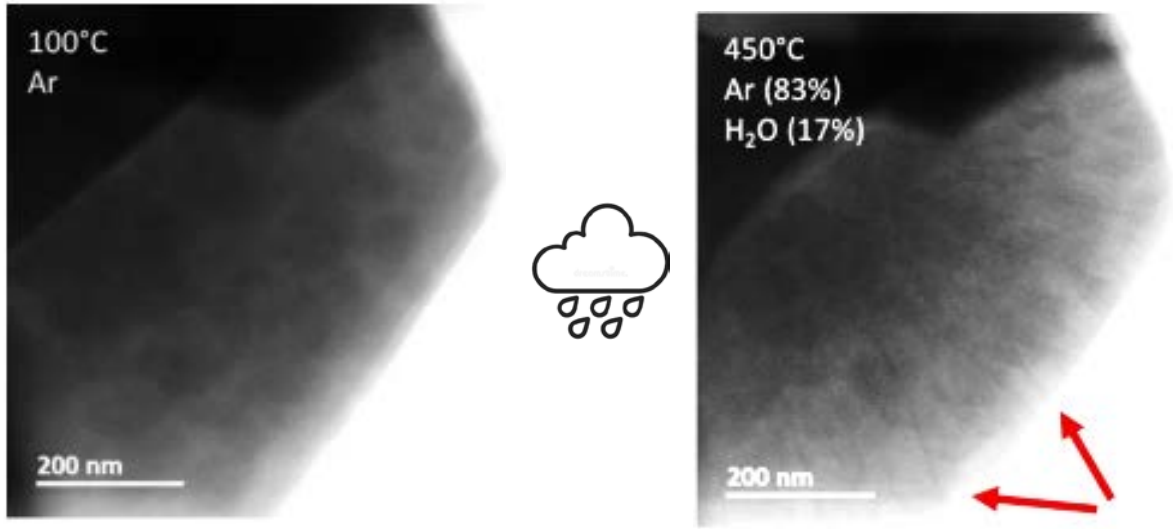
V. Girelli Consolaro

Zeolites

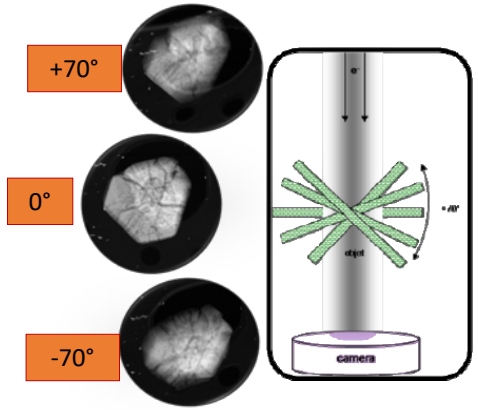




In situ TEM



Electron tomography



- Porous Volume
- Specific Surface
- Types of porosity

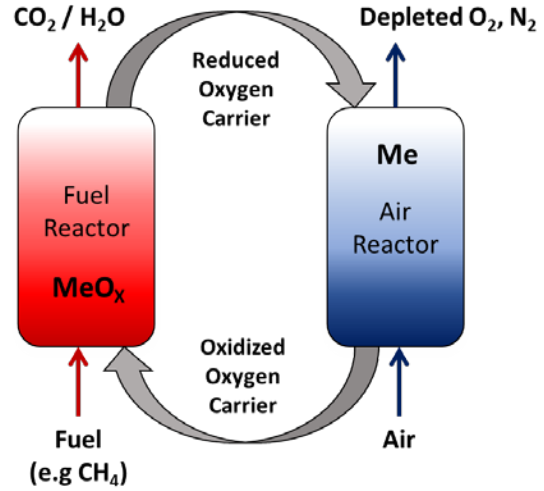
Combine spatial resolution, time resolution and 3D information !

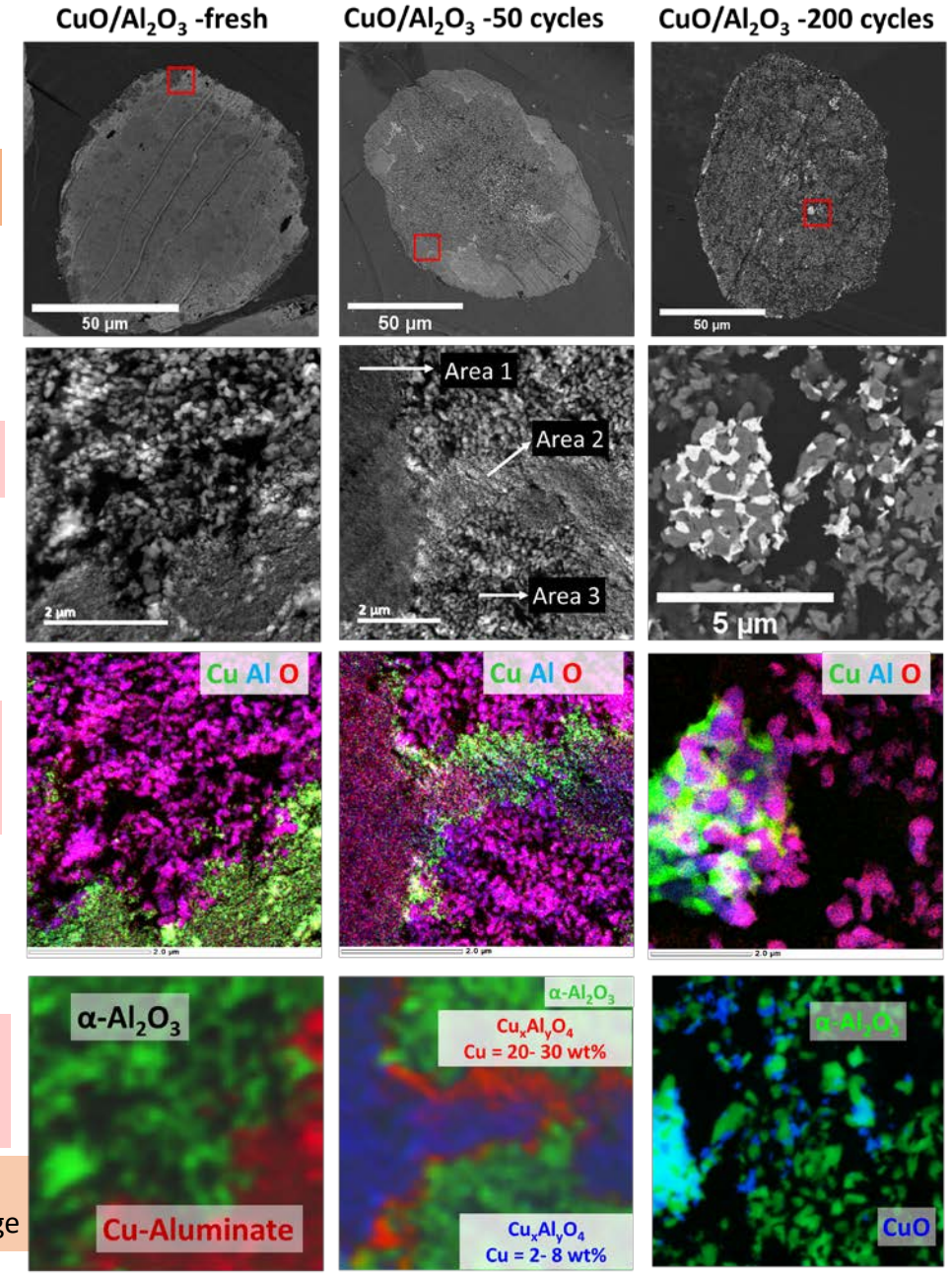
Electron microscopy in CARMEN: correlative study

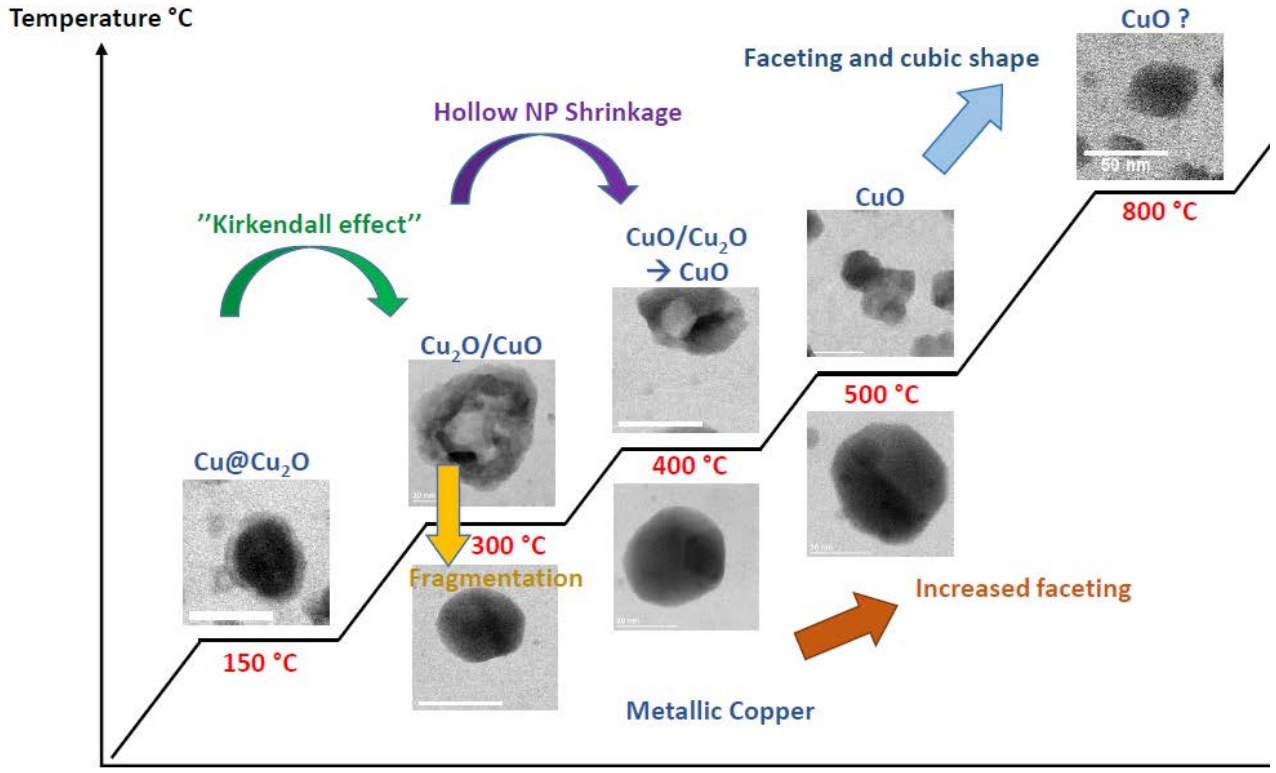
S. A. Sharna

CuO/Al_2O_3 oxygen carriers

Chemical Looping Combustion (CLC)







Electron microscopy in CARMEN: correlative study

S. Vydelingum

TEM experiment

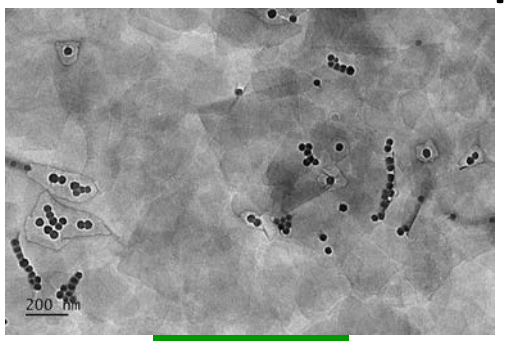


Image 1

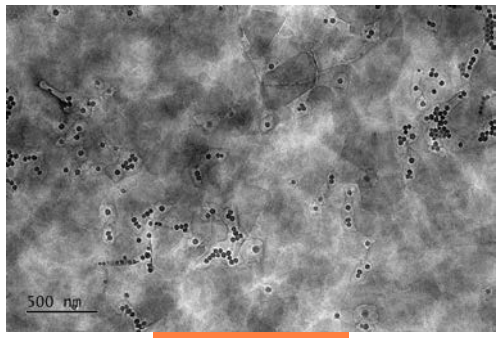
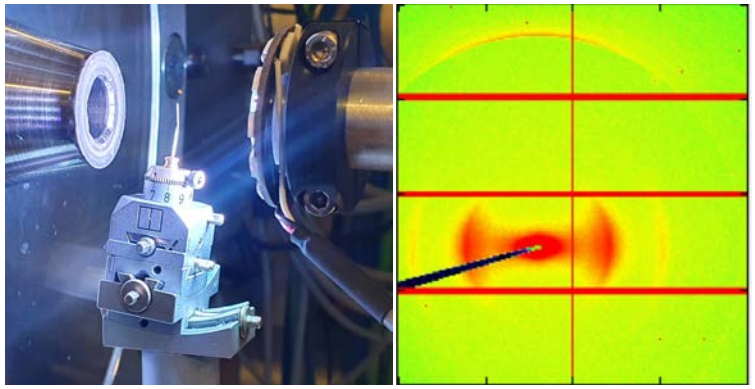
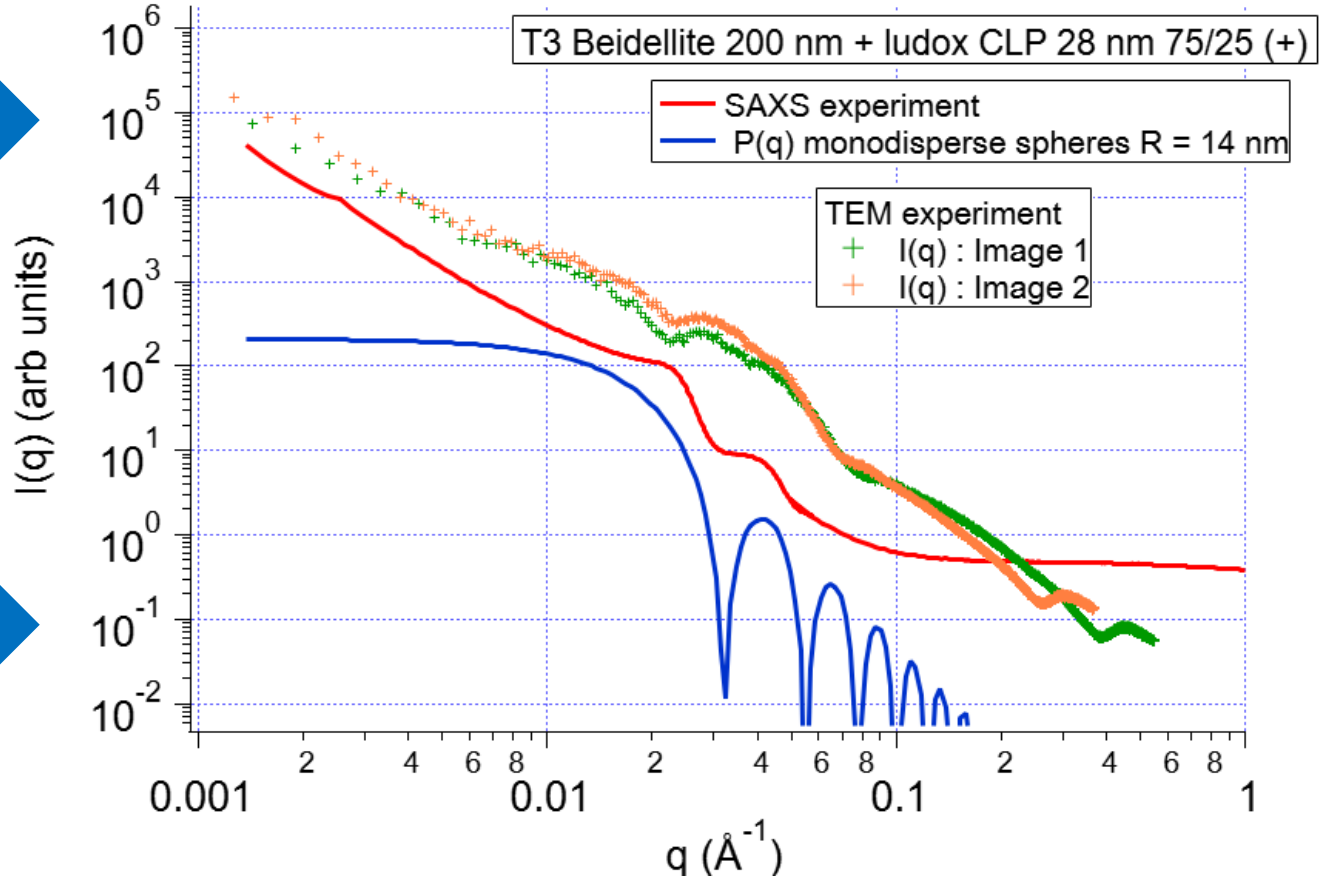


Image 2

SAXS experiment





COMPARISON IN THE RECIPROCAL SPACE

Electron microscopy in CARMEN

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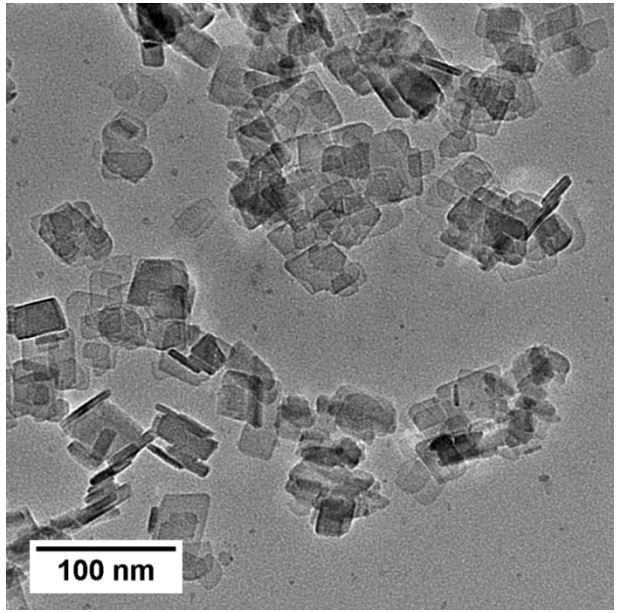
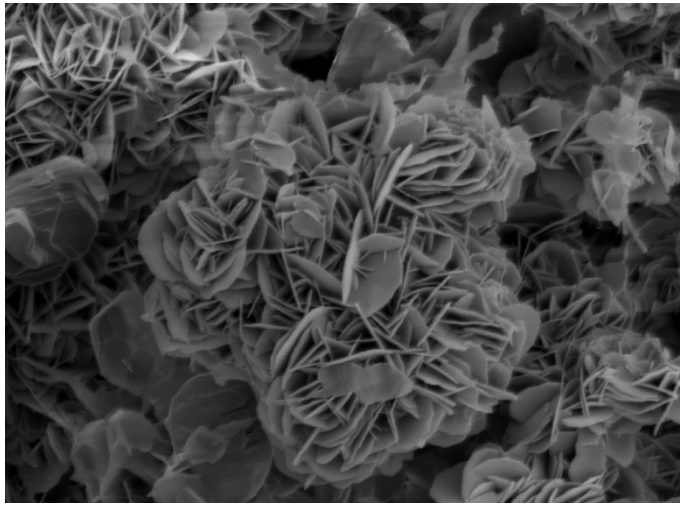
Université de Strasbourg

Bohemite ⇒ Alumina



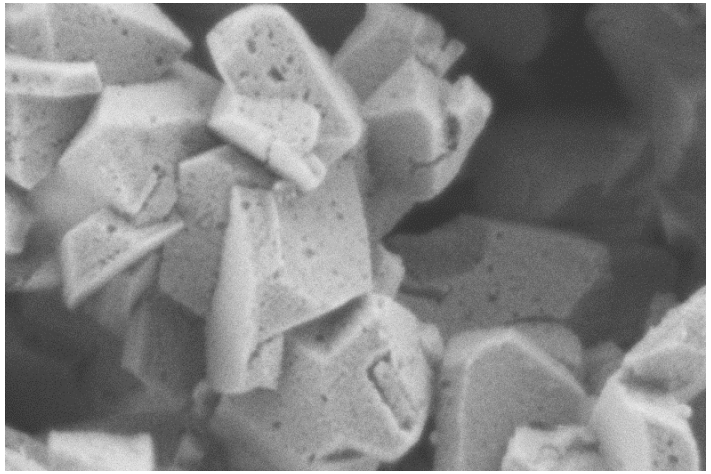
- understanding the formation of the structure

Clay-like systems



- solve the structure and the relative distribution of constituants

Zeolites



- modify the internal structure and the chemical composition

Electron microscopy @ IPCMS


D. Ihiawakrim

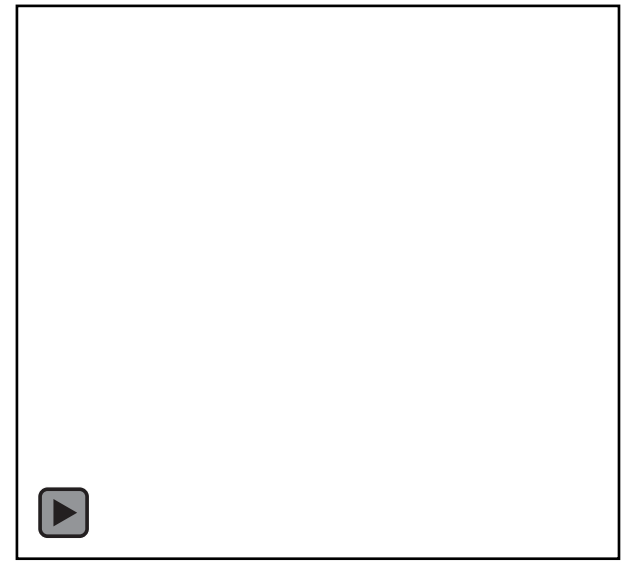

W. Baaziz

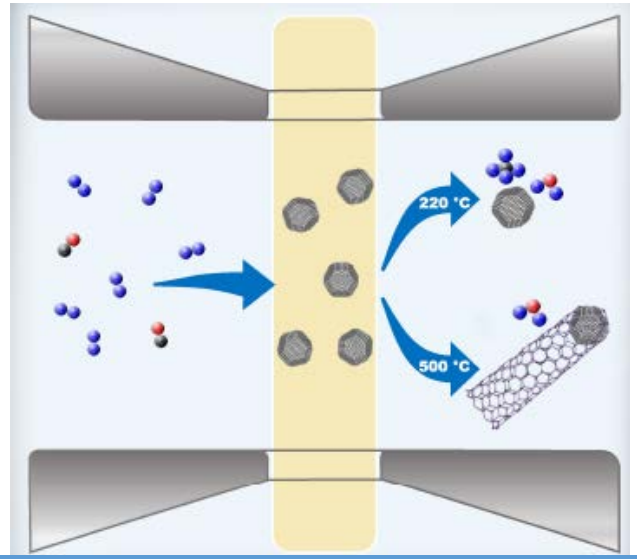

C. Bouillet

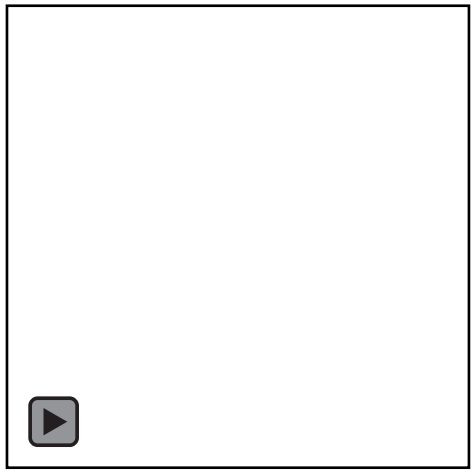

Y. Ramnarain

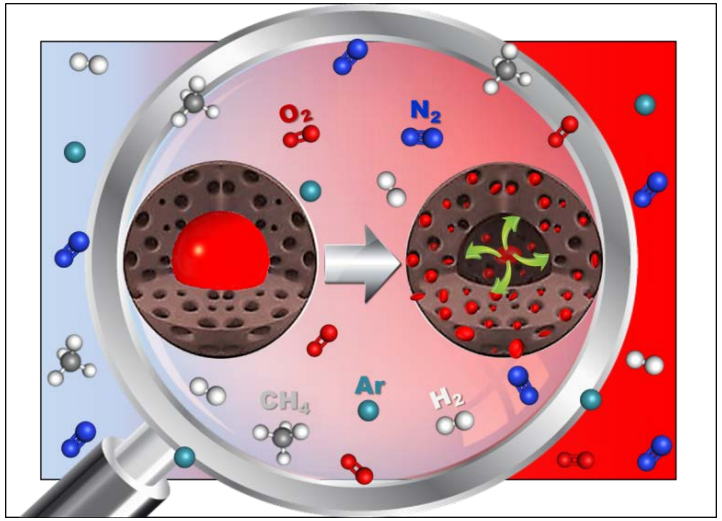

S.A Traore


C. Sidhoum





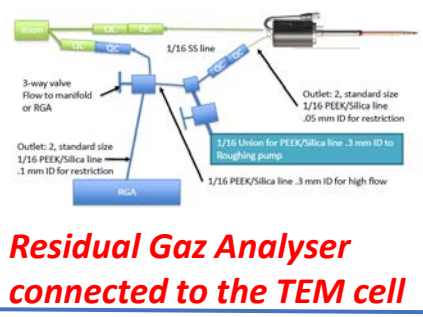




Operando TEM for catalysis

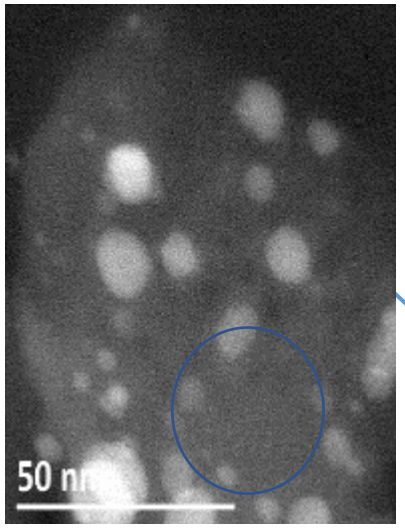
Ni catalysts for CO_2 methanation

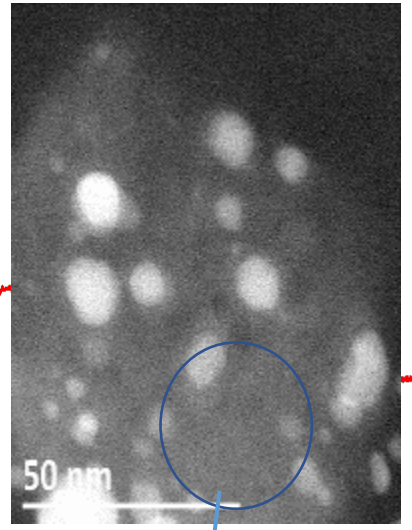
$$CO_2 + H_2 \longrightarrow CO + H_2O \xrightarrow{+3H_2} CH_4 + 2H_2O$$

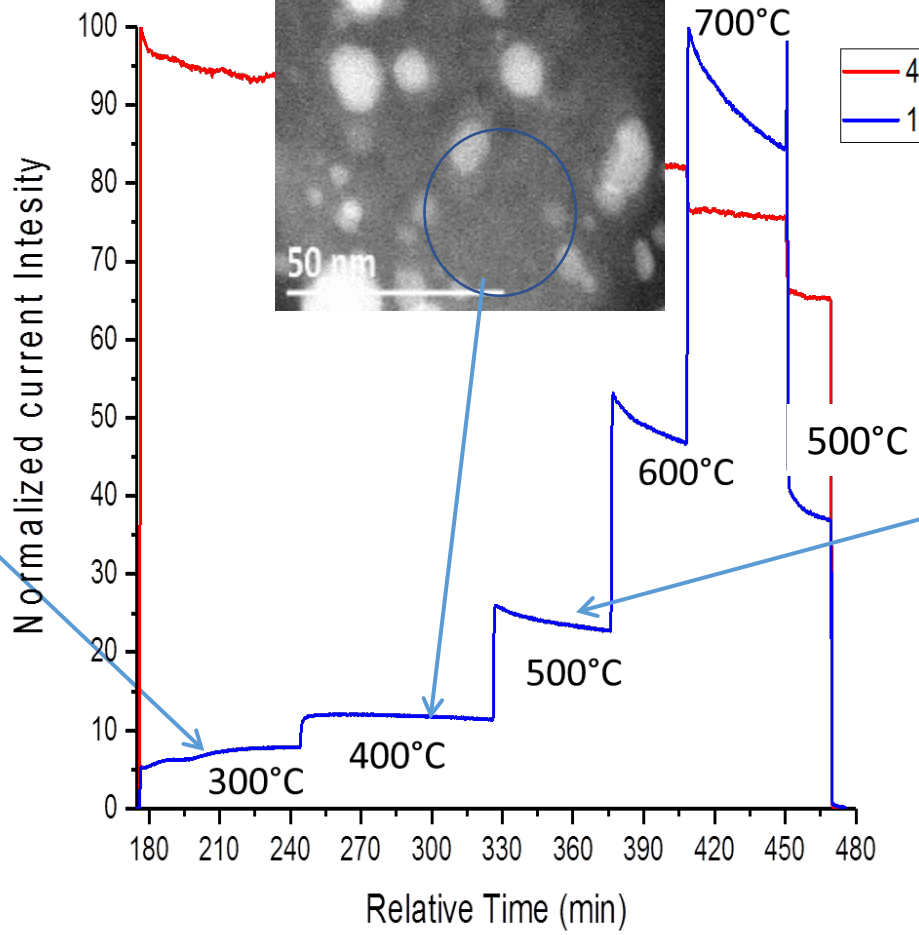


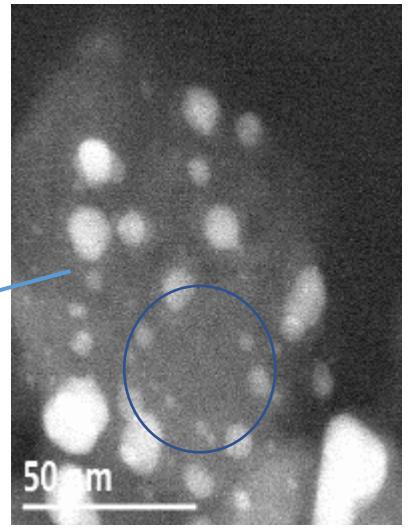
Residual Gaz Analyser connected to the TEM cell

NPs fragmentation

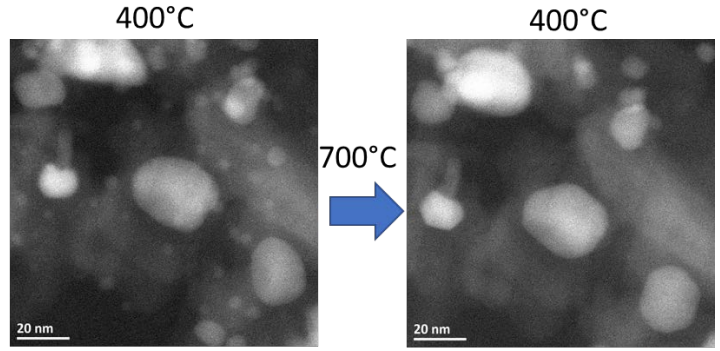


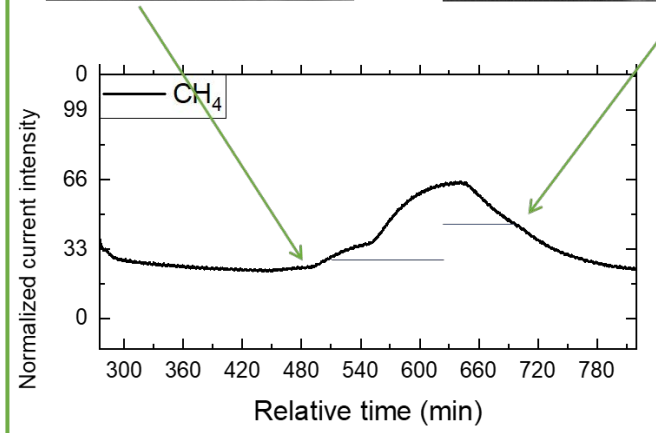






NPs facetting

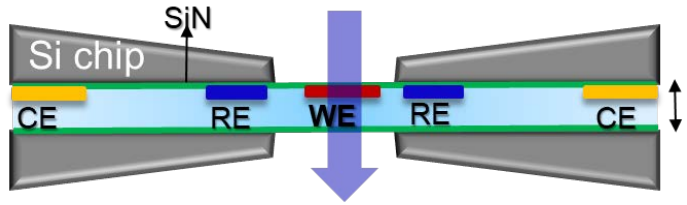




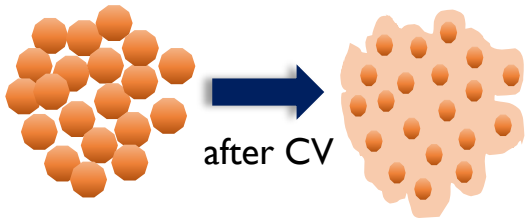
Fragmentation of NPs (presence of water) → higher Co surface → better catalytic activity

Operando TEM for electrocatalysis

Electrocatalysis : in-situ study of nanocatalysts for the HER, OER, RRR reaction

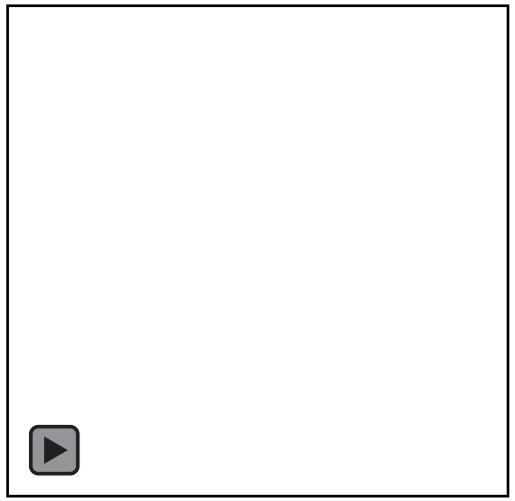


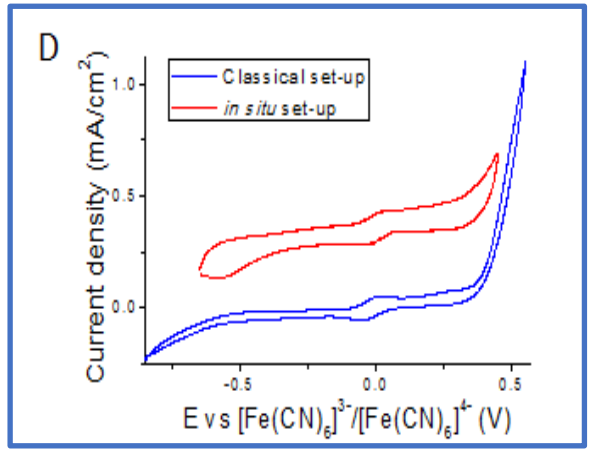
Co_3O_4 nanoparticles



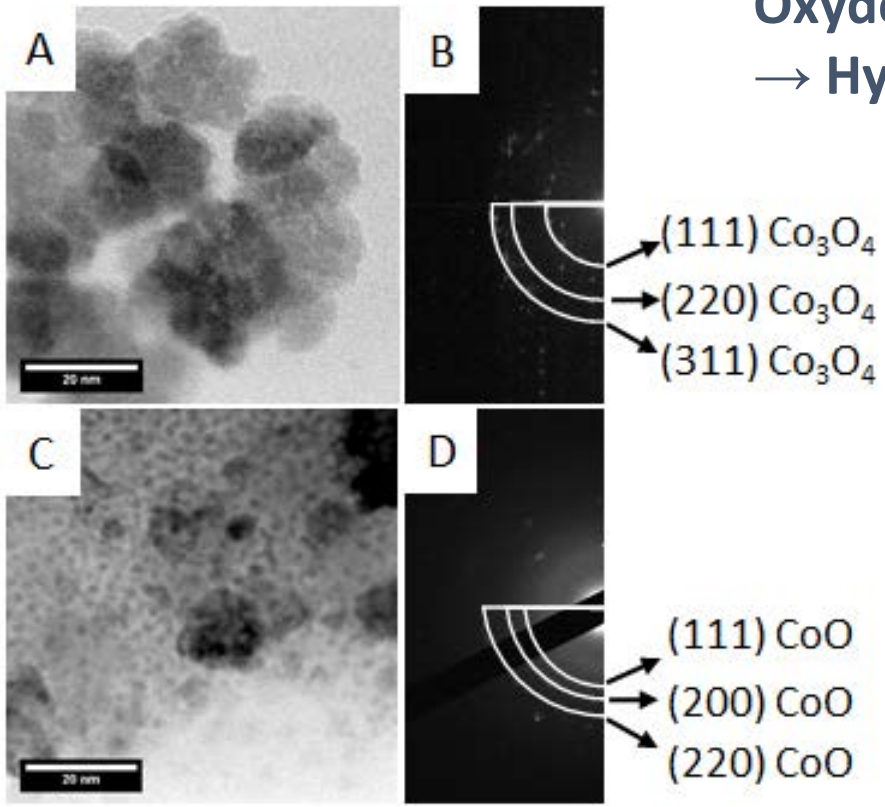
Oxyde
⟶ Hydroxyde

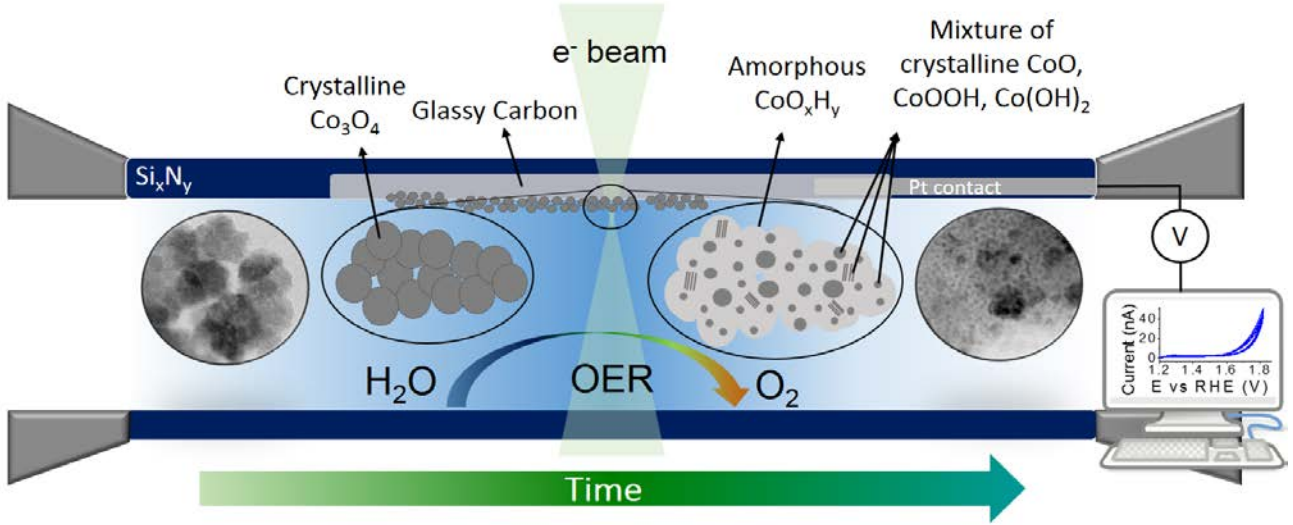
during 1 cycle





structural modifications



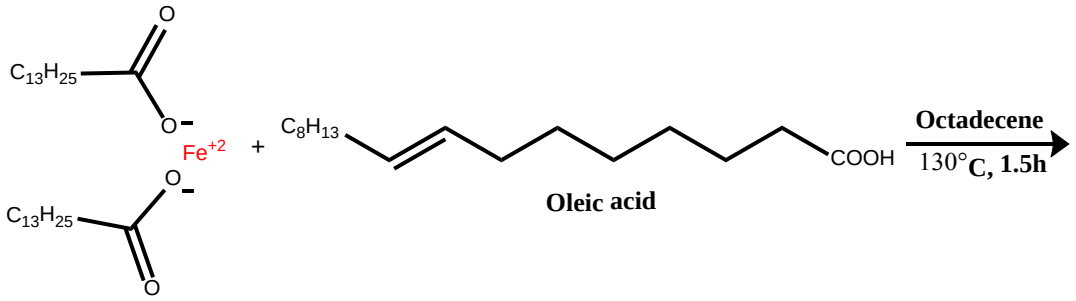


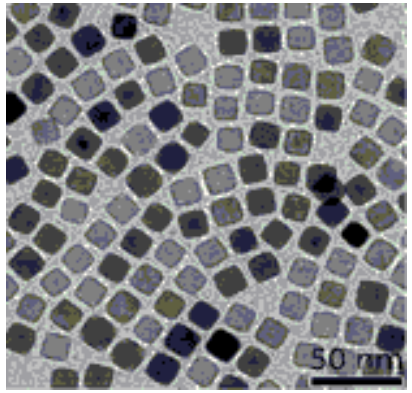
N. Ortiz et al, ***ACS Nano*** *2019*

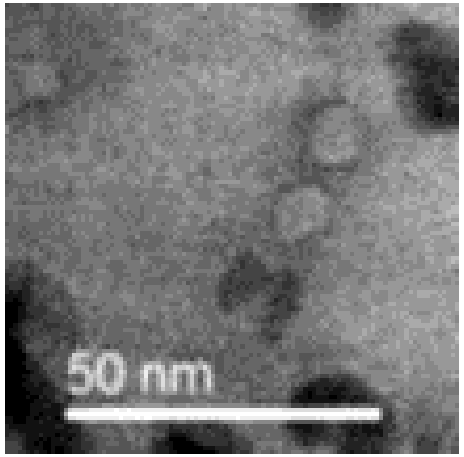
In situ TEM: growth & synthesis processes

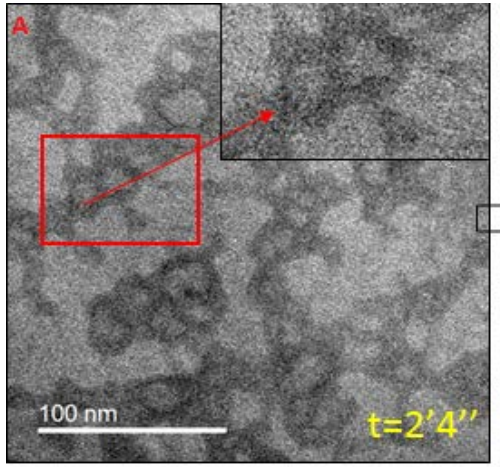
Liquid phase

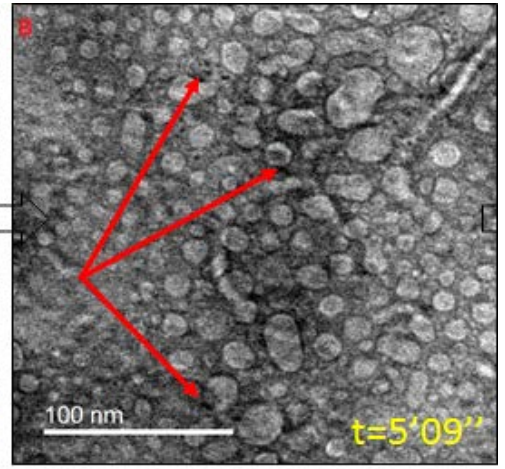
Nucleation and growth of Fe-based NP by *thermal decomposition*

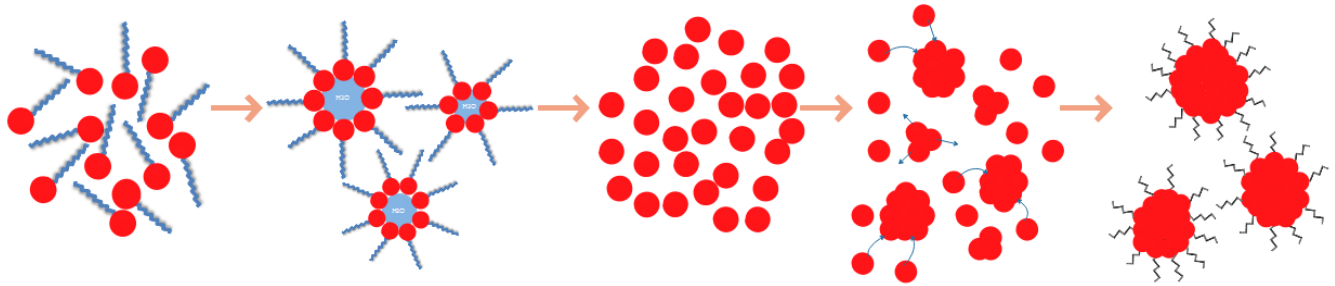












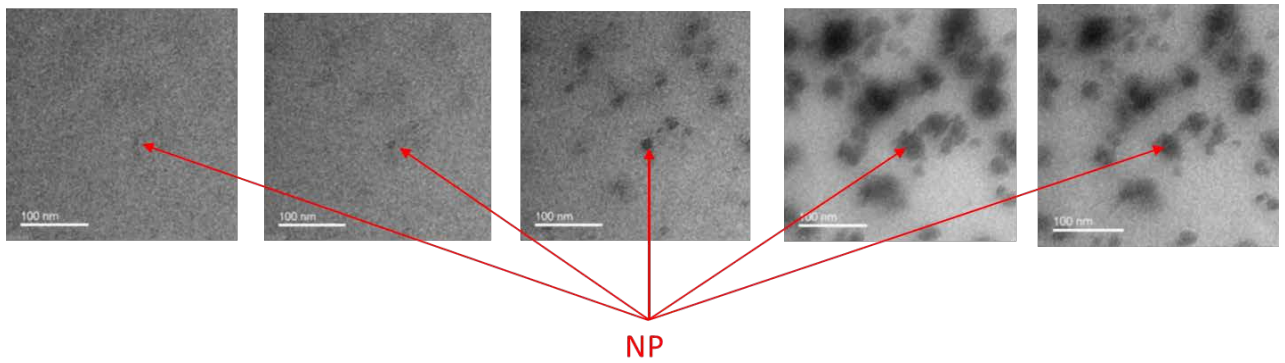
Seed nucleation ↔ ↔ micellar structure

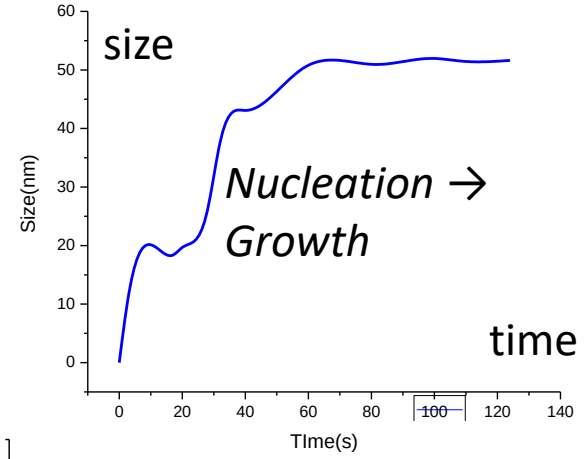
Liquid phase

Nucleation and growth of Fe-based NP by *thermal decomposition*

Energy provided by the electron beam → Decomposition of molecules, Nucleation, Growth

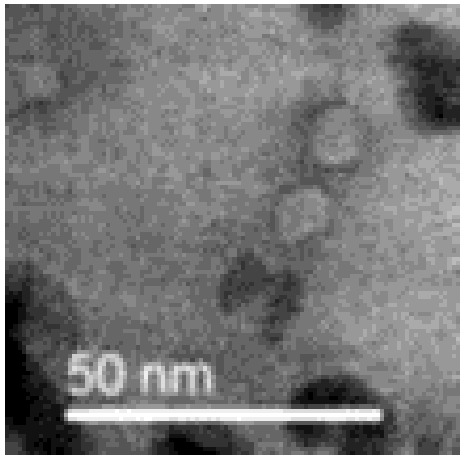
High energy *(electron dose: 250 $e^-/A^2.s$)*

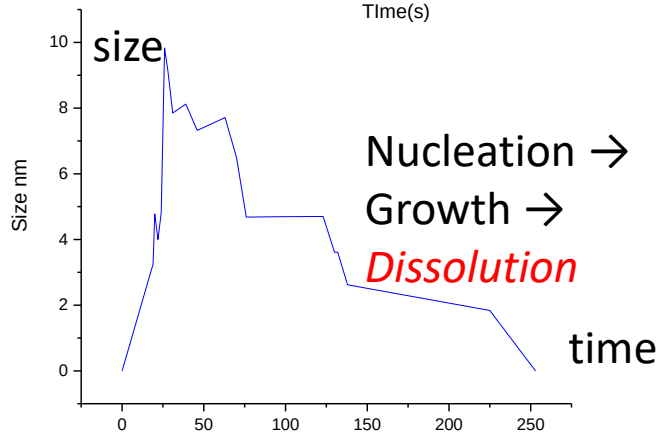




Low energy

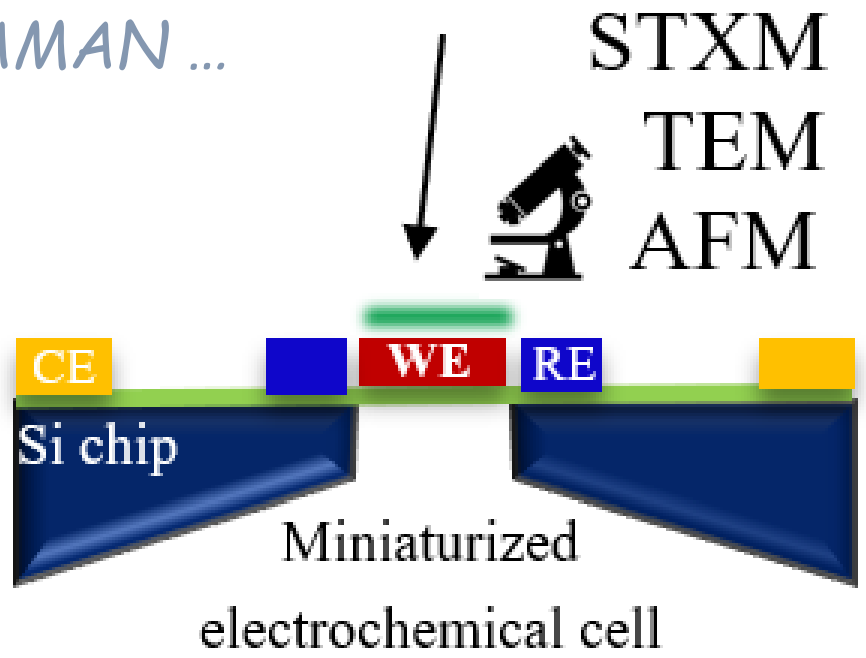
(electron dose: 100 $e^-/A^2.s$)



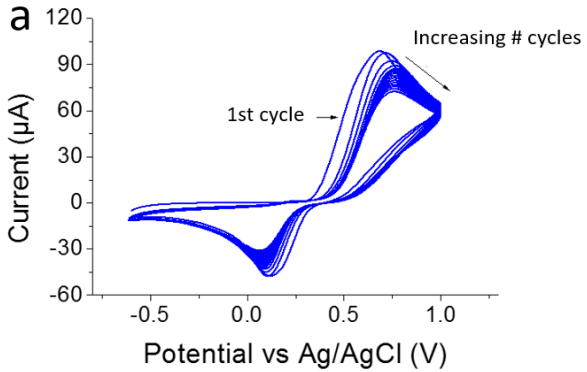


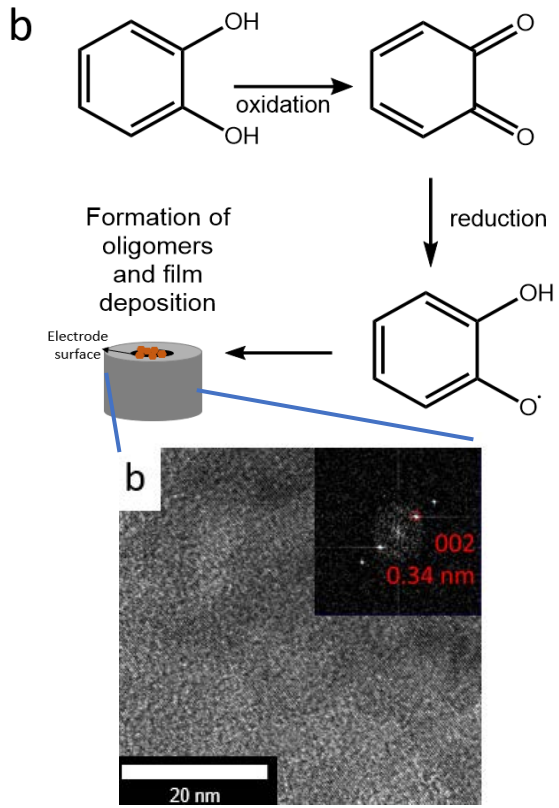
Correlative approaches: *in situ TEM & others techniques:*

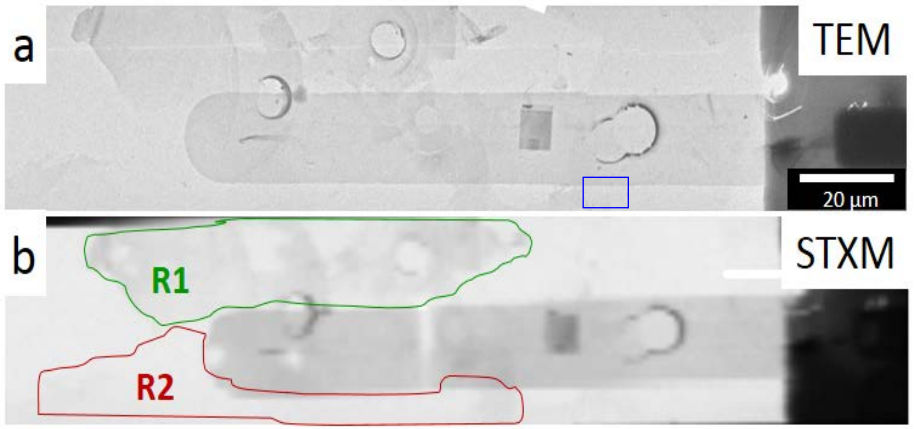
- *X-ray-based: XAS, EXAFS, STXM …*
- *other imaging modes: AFM …*
- *spectroscopies: RAMAN …*



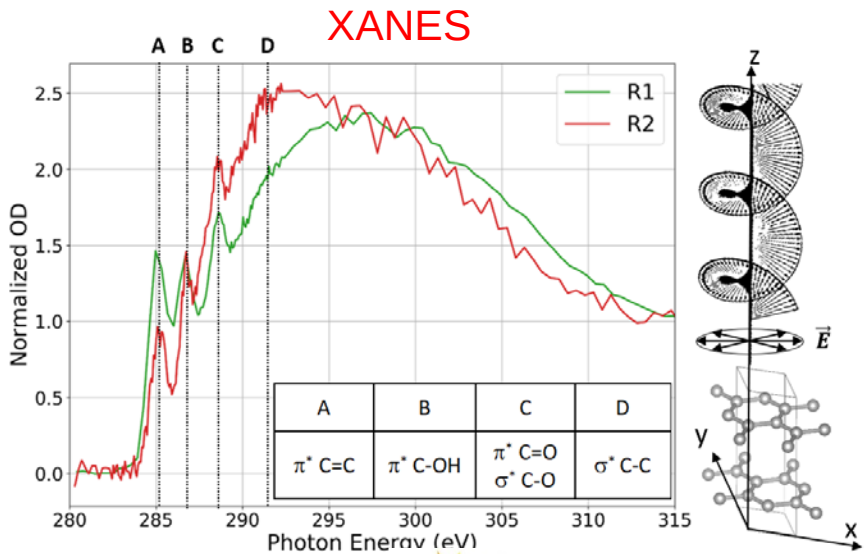
Correlative Insight on Electrodeposited Graphite Oxide Films







N. Ortiz Pena et al, J Phys Chem Letters 2020



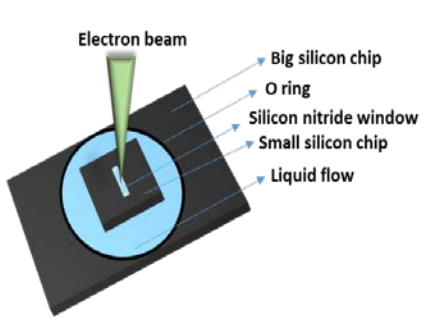
S. Stanescu

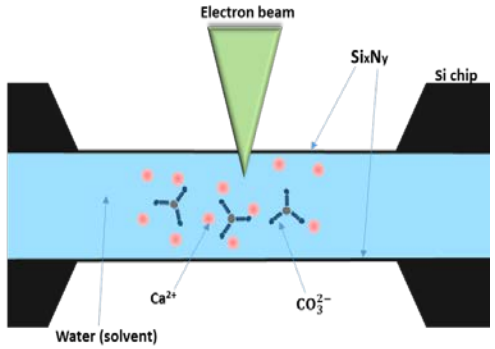
Nucleation and growth of $CaCO_3$: influence of L-asp

Coll. T. AZAIS
(LCMCP Paris)

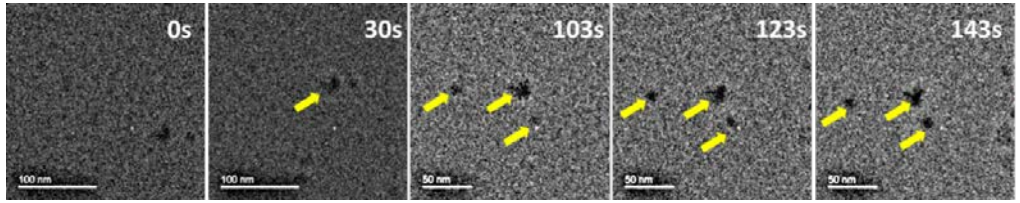
V. Ramnarain

Liquid phase TEM

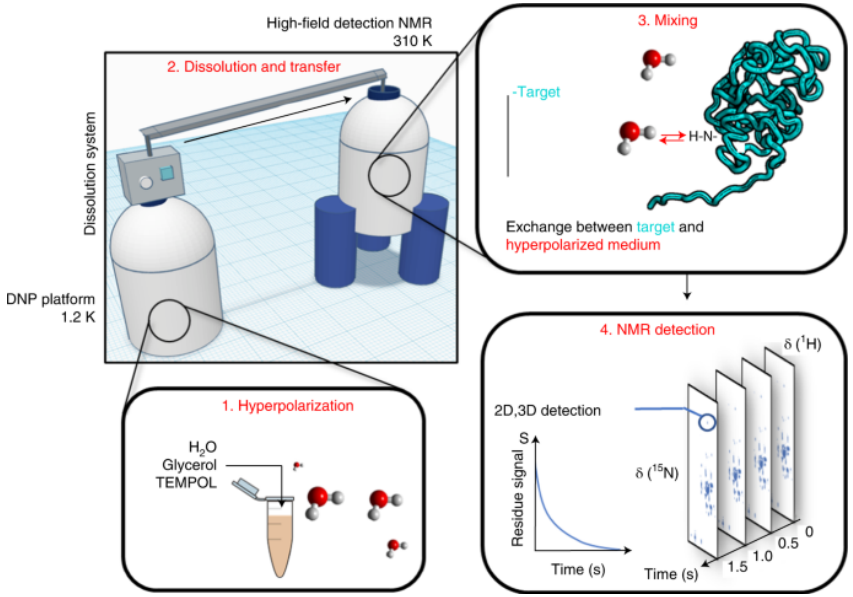




Real time visualisation of prenucleation events



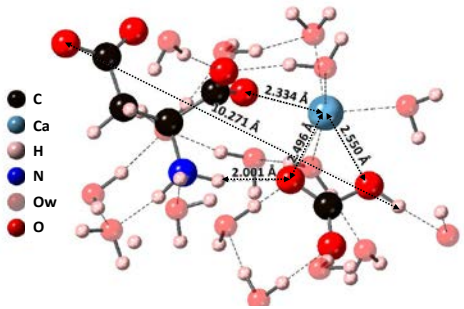
Hyperpolarized NMR

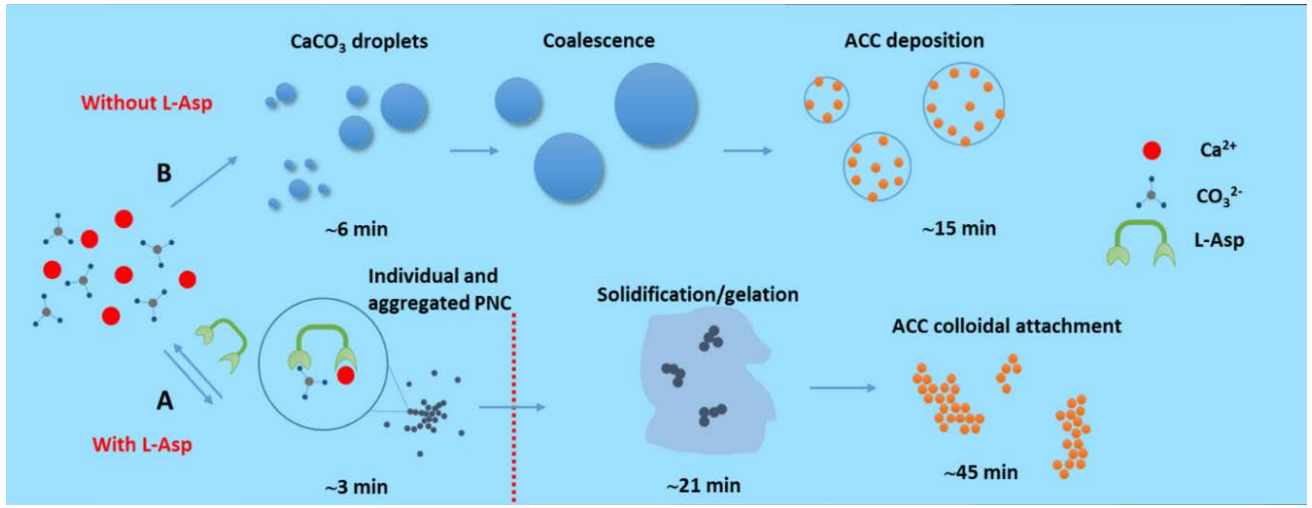


Structural characterization of prenucleation species

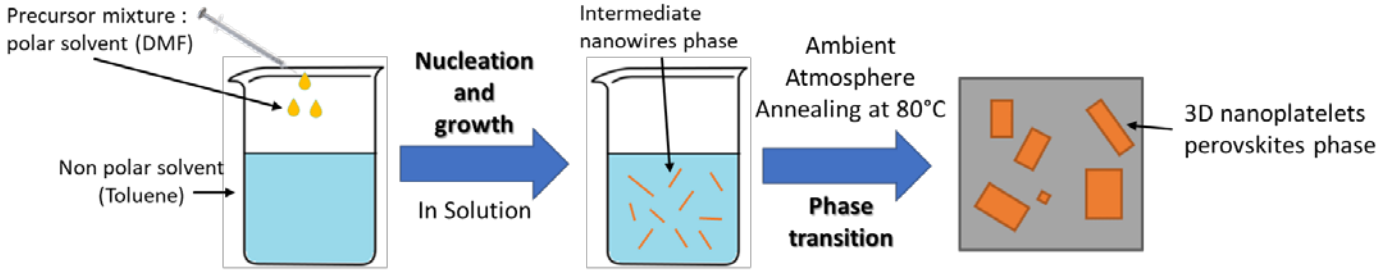
+ Ca^{2+} potentiometric titrations

+ DFT calculations

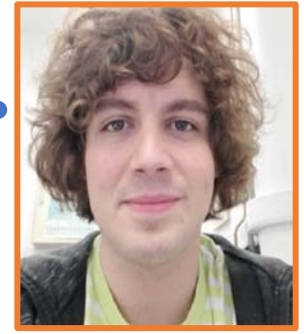




Growth of hybrid perovskites: a correlative study

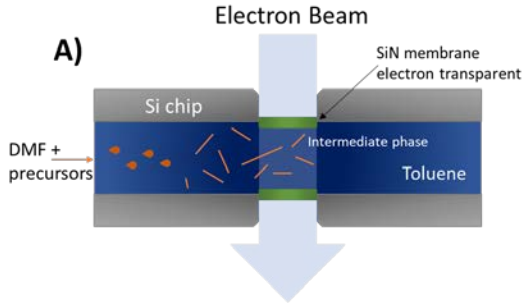


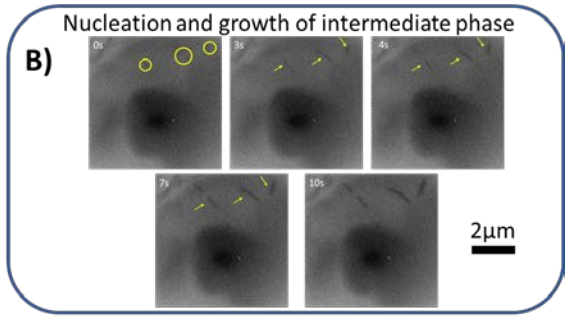
Coll. C. SANCHEZ
(USIAS, LCMCP Paris)

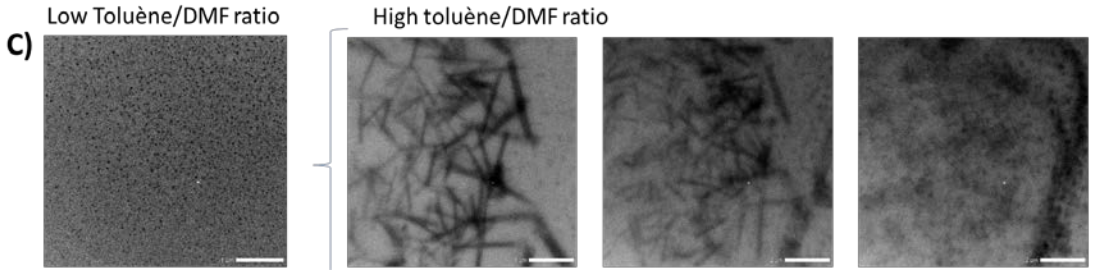


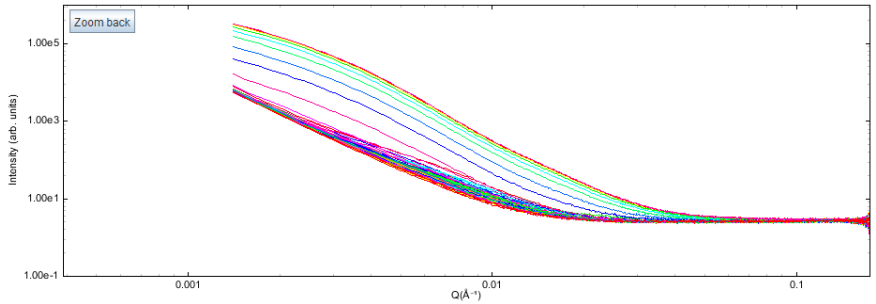
C. SIDHOUM

Liquid In Situ TEM & SAXS (SOLEIL)

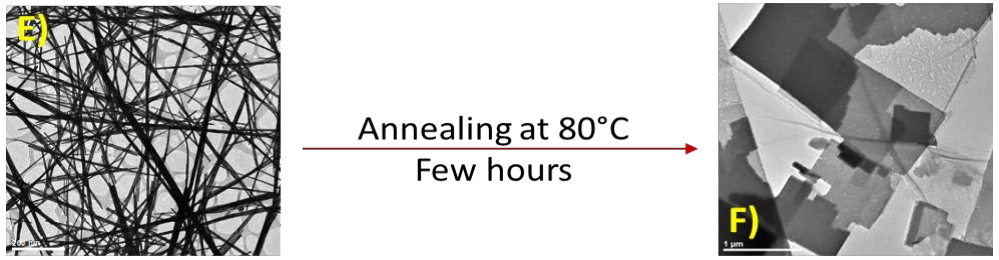


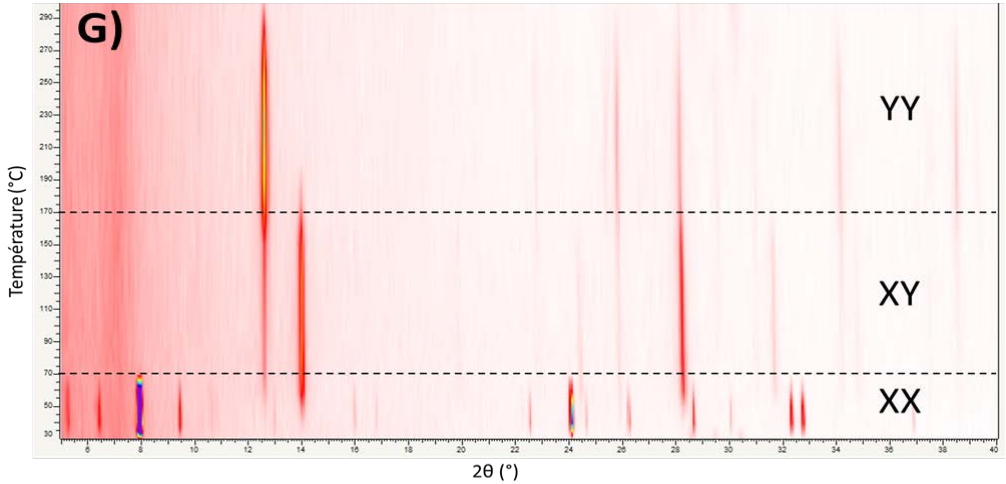






Gas In Situ TEM & In Situ XRD



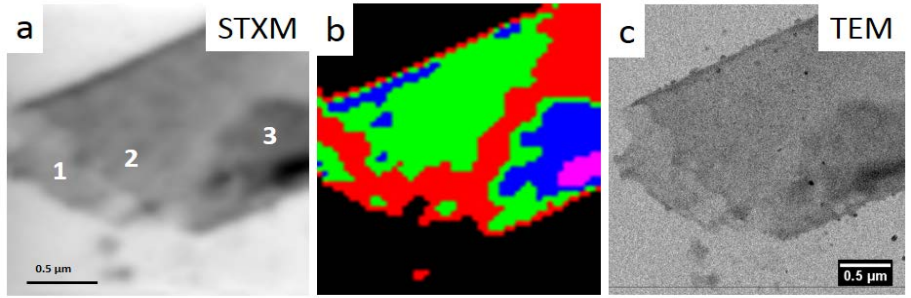


- XX : Intermediate phase MAI – PbI_2 – DMF
- XY : 3D Perovskite MAPI
- YY : Decomposition into PbI_2

In situ TEM: new developments and perspectives

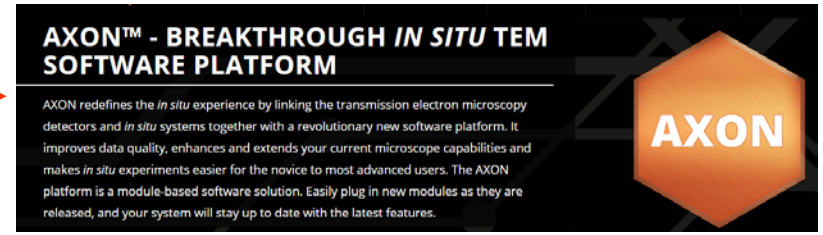
Data acquisition:

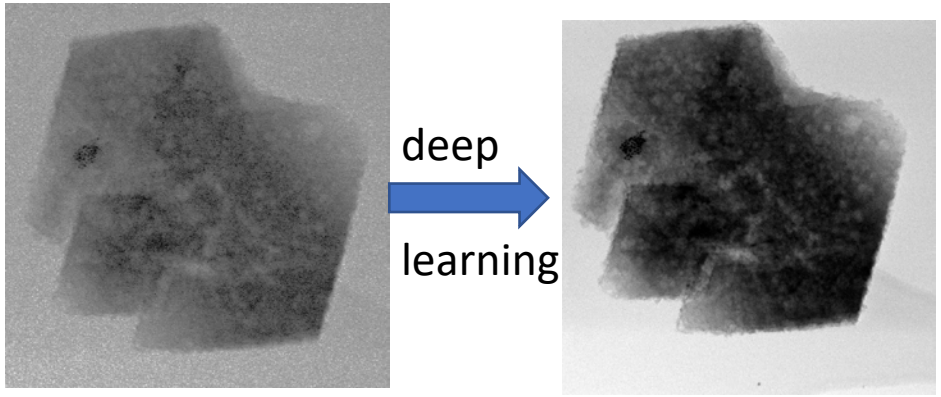
- new detectors
- correlative approaches: TEM + STXM



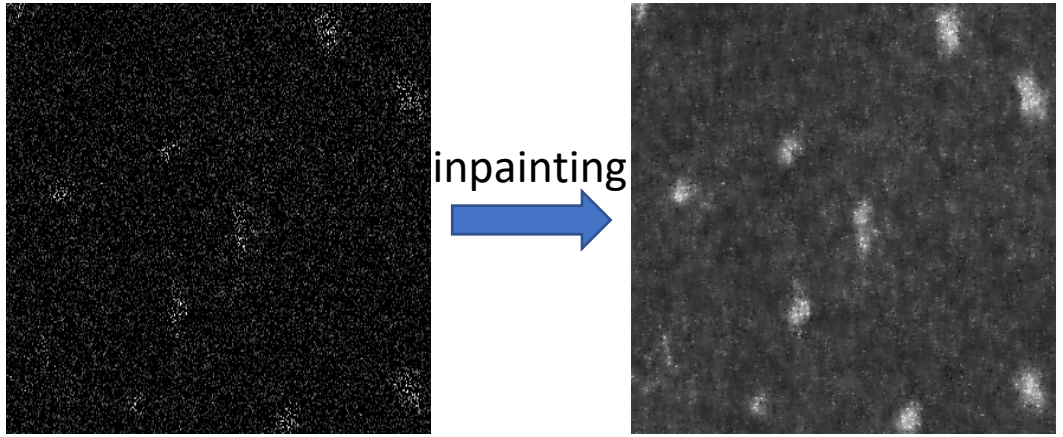
Reducing electron dose and beam influence

- dedicated acquisition software for “in situ”
- “inpainting” methods
- deep learning approaches





Coll. M. Moreaud, IFPEN



Coll. N. Browning, Liverpool

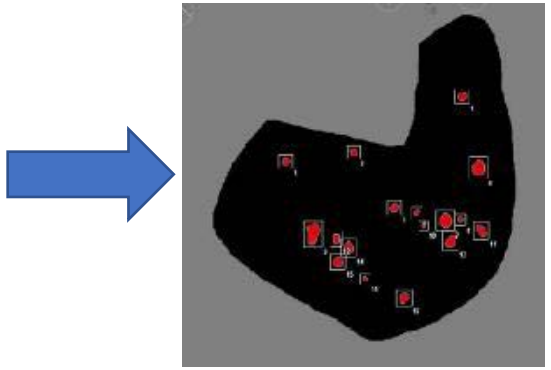
In situ TEM: new developments and perspectives

Data analysis

➢ Deep learning approaches to manage a large amount of data and provide

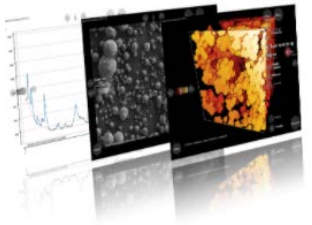
a) quantitative results

b) statistically representative information



bel	Area (pixels)	Mean Diameter (pixels)	Standard Deviation Diameter	Min Diameter (pixels)	Max Diameter (pixels)	Max Min Diameter Ratio	Elongation(D*D/A)
1	202	15,18	1,1	13,42	17,89	1,33	1,58
2	125	11,74	1,26	8,94	14,42	1,61	1,66
3	164	13,61	1,44	10,77	16,49	1,53	1,66
4	492	24,23	2,79	20	30,27	1,51	1,86
5	199	15,04	1,32	12,65	17,89	1,41	1,61
6	91	9,94	1,24	8	12,81	1,6	1,8
7	447	23,09	2,45	19,7	28,64	1,45	1,83
8	94	10,06	0,76	8,25	11,66	1,41	1,45
9	648	29,73	9,94	18,87	50	2,65	3,85
10	46	6,81	0,79	5,66	8,25	1,46	1,48
11	267	18,34	4,51	11,66	27,78	2,38	2,89

x N images



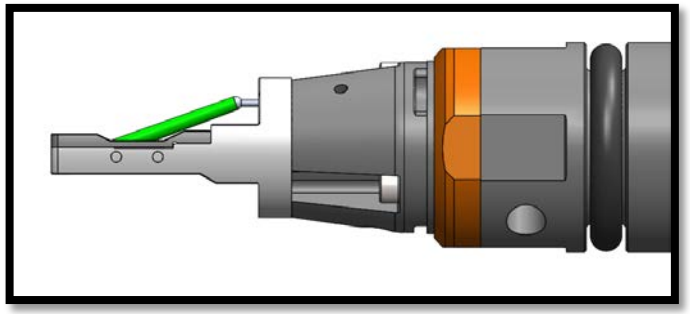
Coll. M. Moreaud, IFPEN

Deep learning – based data analysis

In situ TEM: new developments and perspectives

Instrumental developments

- Development of new specimen holders

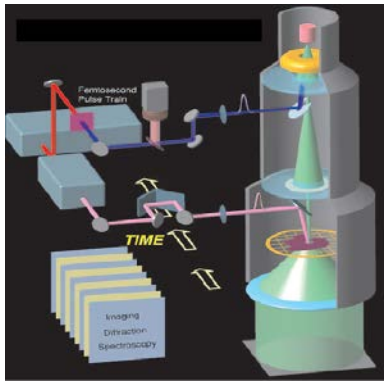


Optical environmental holder

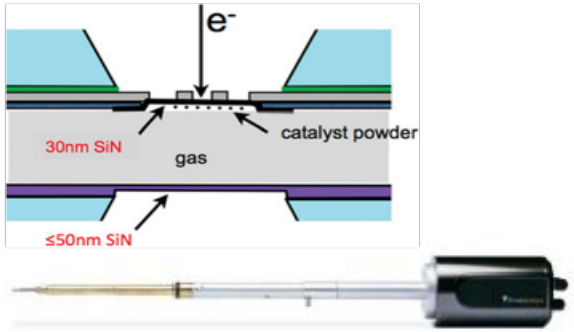
specimen in gas or liquid and under light exposure

- Combining spatial and time resolution ⇒ kinetics of processes (Brownian motion)

  ⇒ dynamic of nano-objects in specific environments

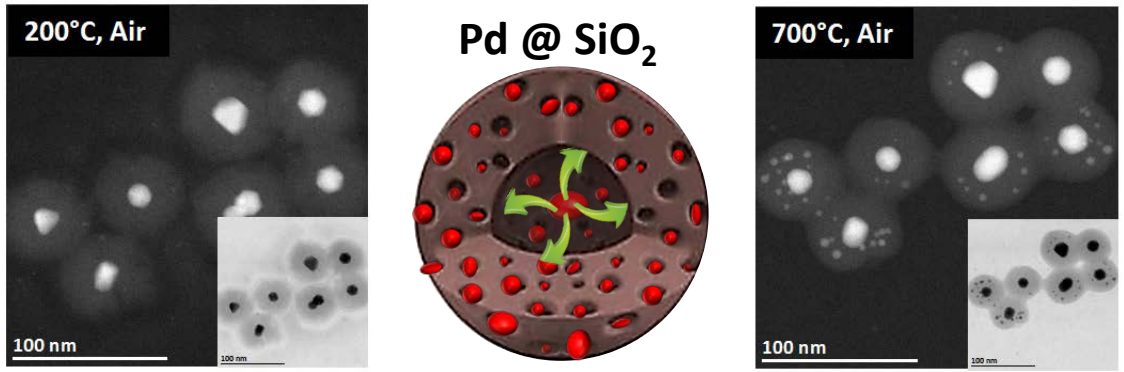


UTEM + ETEM

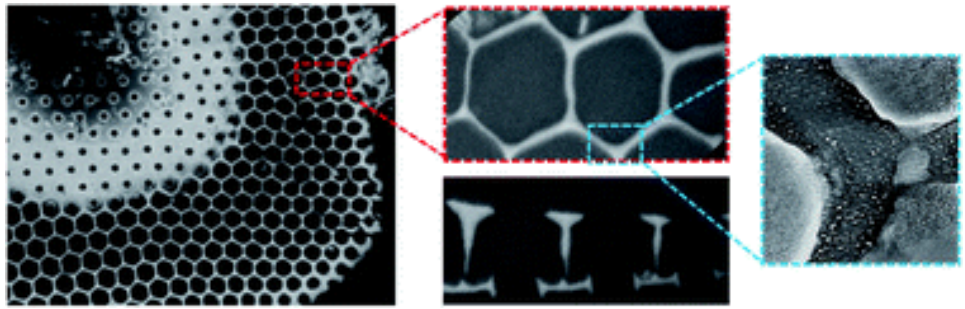


TEM: very useful, multi-task characterization tools in material science

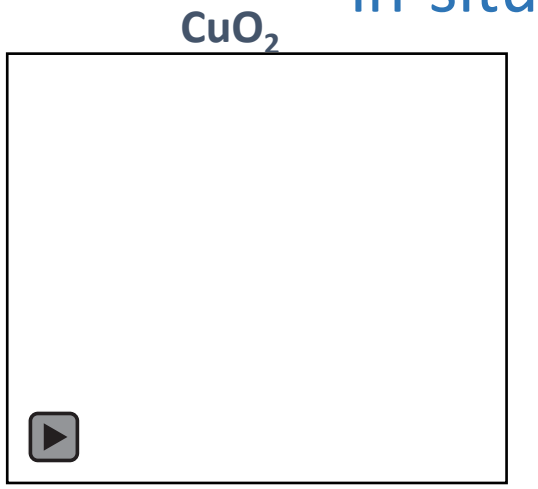
combined spatial and time resolution

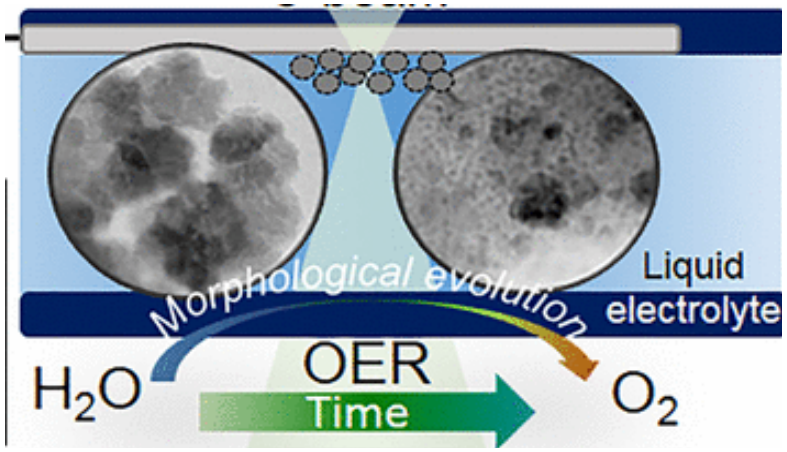


mutiscale analysis

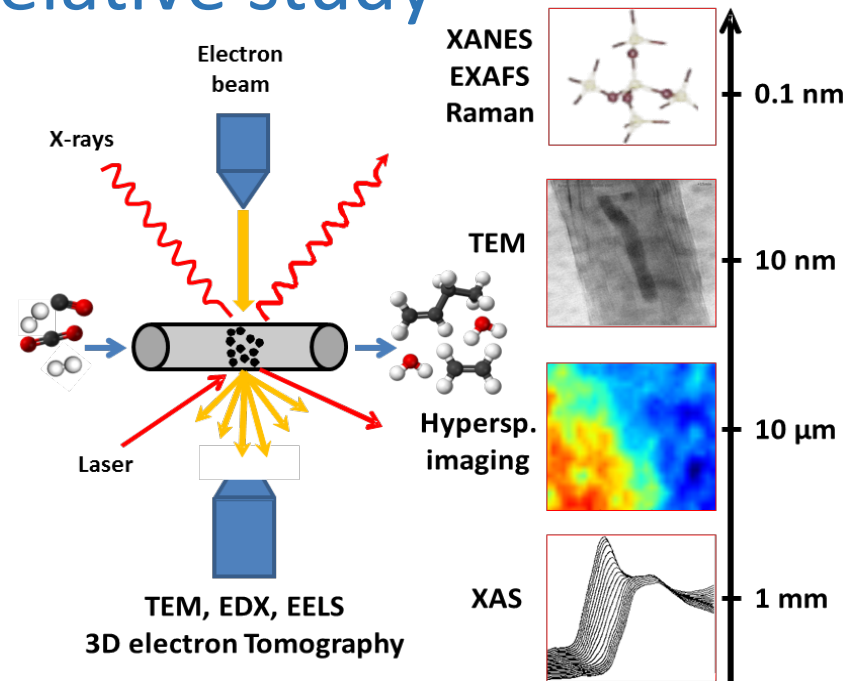


in-situ and operando technique





correlative study



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- Synthesis, properties of nanomaterials: *IPCMS, LCMCP (Paris) …*
- Heterogeneous catalysis : ***IFPEN (Lyon), UCCS (Lille), ICPEES (Strasbourg)***
- Biomaterials : *Federal University of Rio de Janeiro (Brazil)*
- Characterization by X-ray based techniques: *SOLEIL*
- Electron microscopy: *CCEM (Hamilton, Canada), INA (Zaragoza)*
- In-situ TEM holders: *Protochips, Eden Instruments*

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