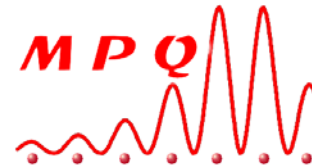


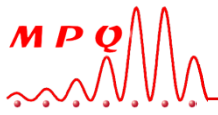
Exploring new frontiers in materials with Aberration Corrected Electron Microscopy

Christian RICOLLEAU

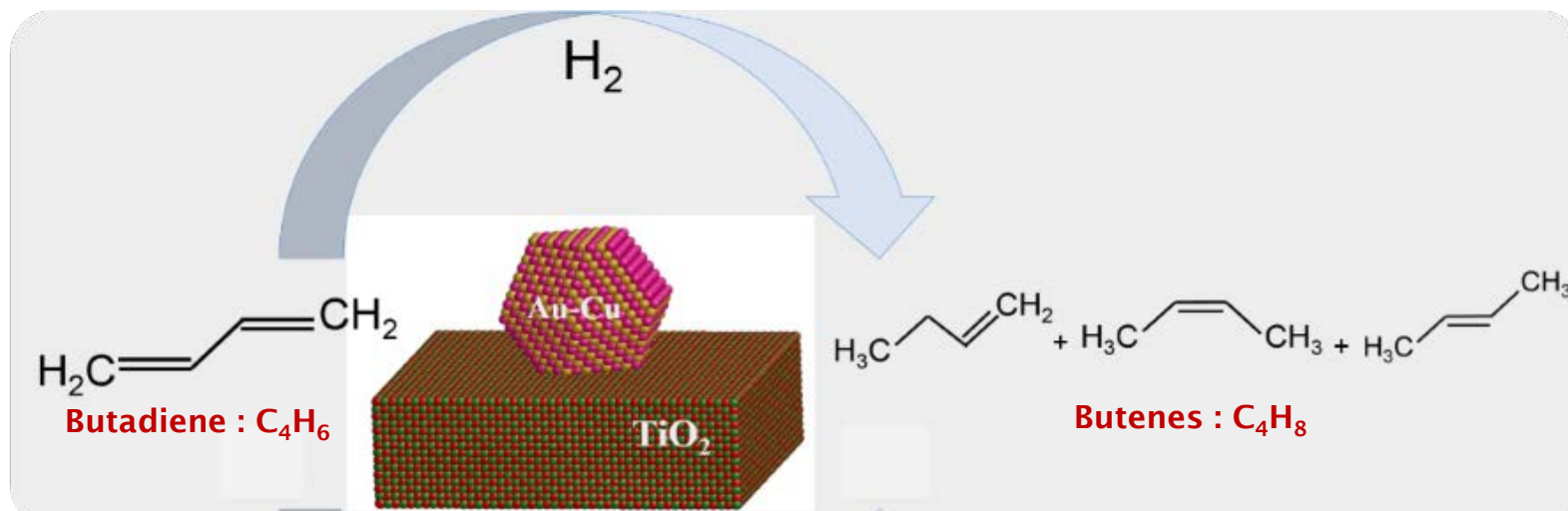
**Jaysen Nelayah, Damien Alloyeau, Guillaume Wang
and Hakim Amara (also at LEM, CNRS / ONERA)**

Me-ANS

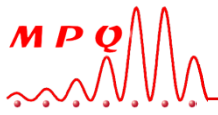




1. Heterogeneous catalysis in operando Transmission Electron Microscopy: toward single particle analysis
2. Electron microscopy in liquid: multiscale approach and correlation between nanoparticles growth and optical properties
3. High Entropy Alloy: new class of complex material for hydrogen storage



Gain fundamental real time atomic-scale insights into the interplay between structure and catalytic properties of heterogeneous catalysts by *operando* transmission electron microscopy (TEM)

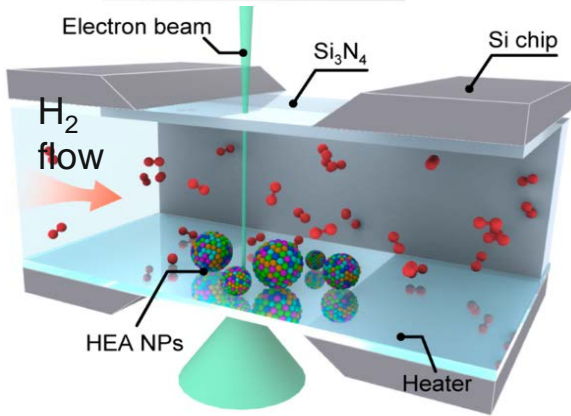


Set up and optimization of residual gas analyzer on the AC-TEM

CARMEN Symposium: Evolution

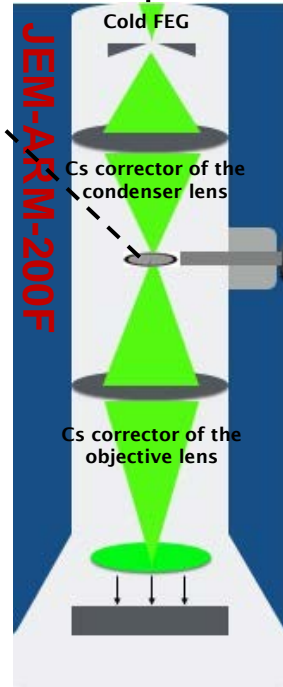
Protochips Atmosphere™
TEM environmental high-pressure gas cell

Planar (vertical) nanoreactor



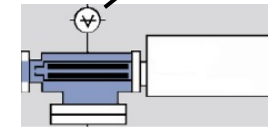
- *In situ* temp : up to 1200 °C
- Pressure: up to 1 atm
- $m_{\text{cat}} = \sim \text{ng}$
- $V_{\text{gas}} = \sim \mu\text{l}$

Super TEM 2



Residual gas analyzer
(RGA ,PrismaPro)

High precision valve
(UDV 40)



Mass spectrometer

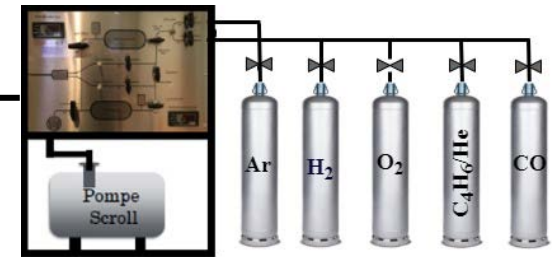


Turbopump (HiPace 80)

Diaphragm pump
(MVP 040-2)

Elimination of mechanical vibration
induced by the turbomolecular pump

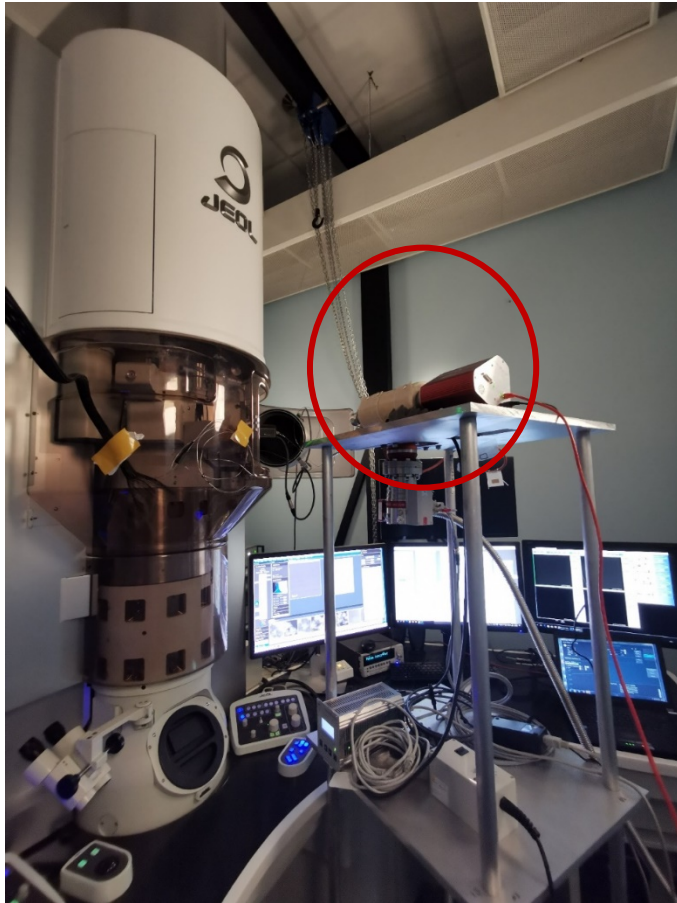
Manual gas distributor



Challenge :

Achieve a high sensitivity for trace gas detection

Keep the atomic resolution of Super TEM



PrismaPro® by PFEIFFER

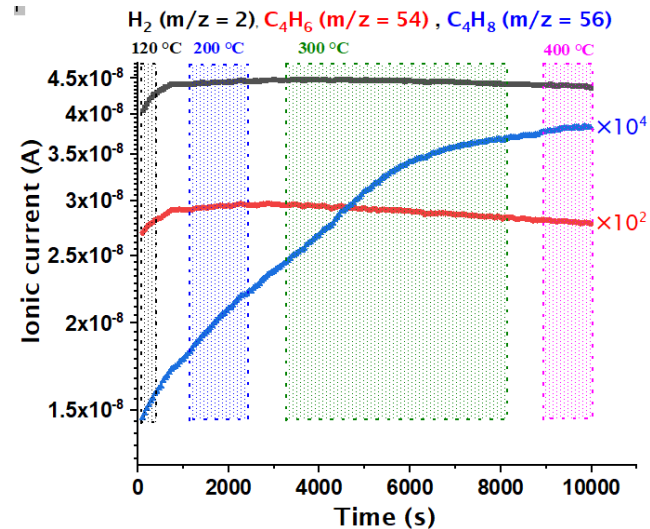
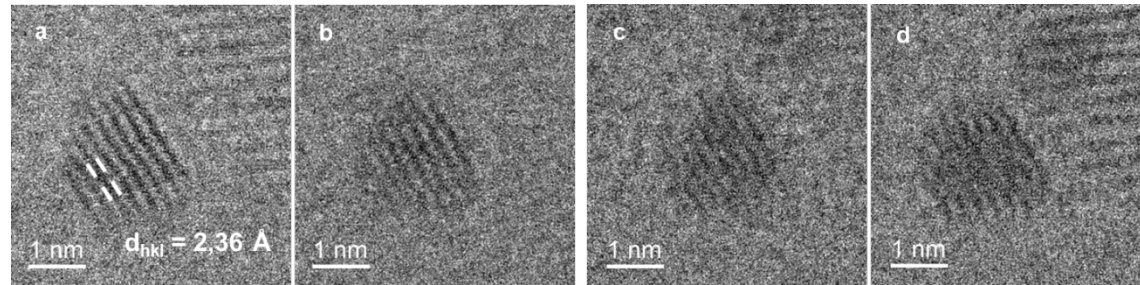
Mass range: **1-100 amu**

Detector : Faraday/ C-SEM

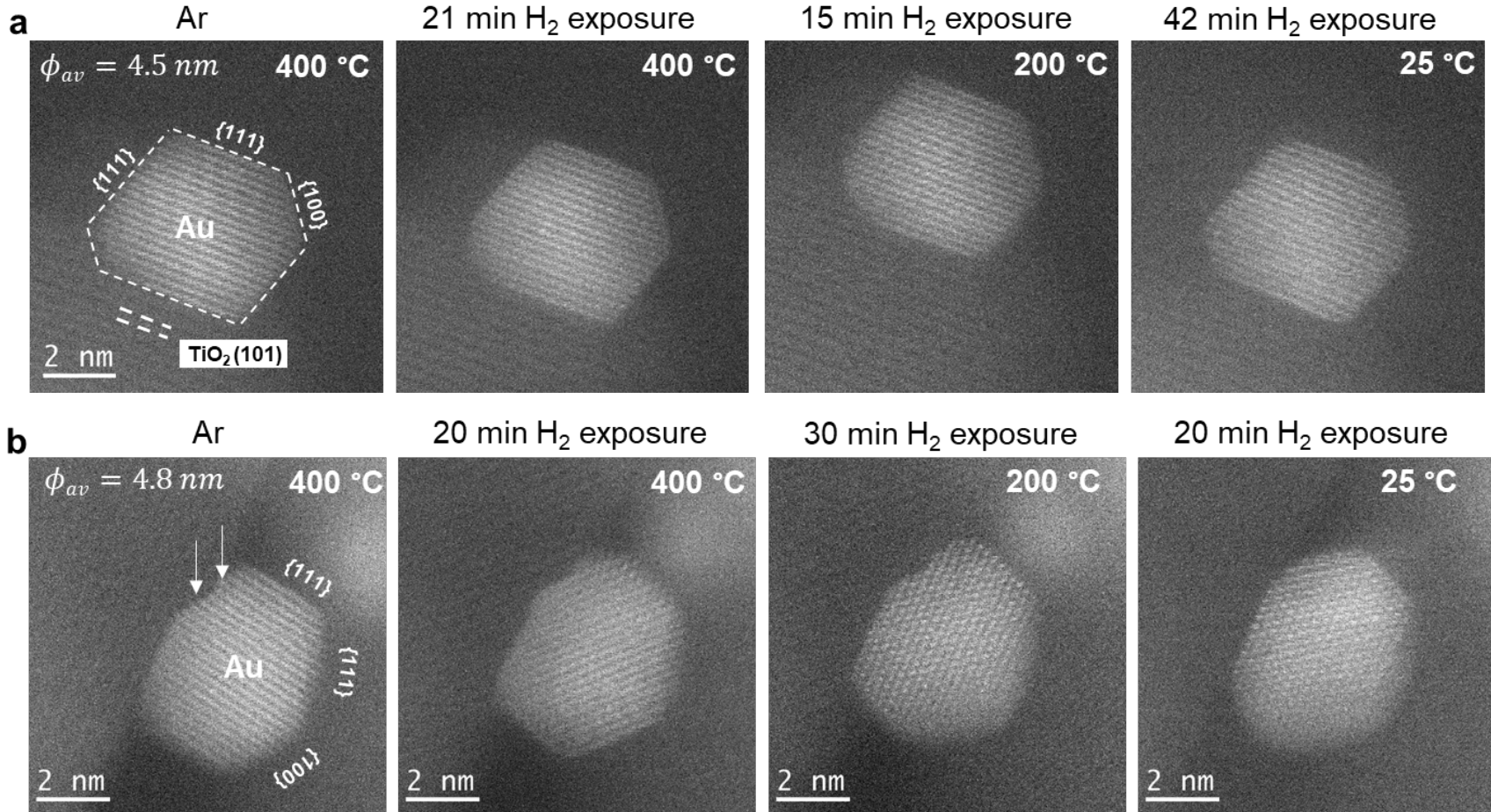
Operating pressure max : $5 \cdot 10^{-4}$ mbar

Detection limit min : $4 \cdot 10^{-13}$ mbar

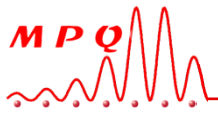
Au NP in butadiene hydrogenation reaction



Atm pressure : Static H₂ environment

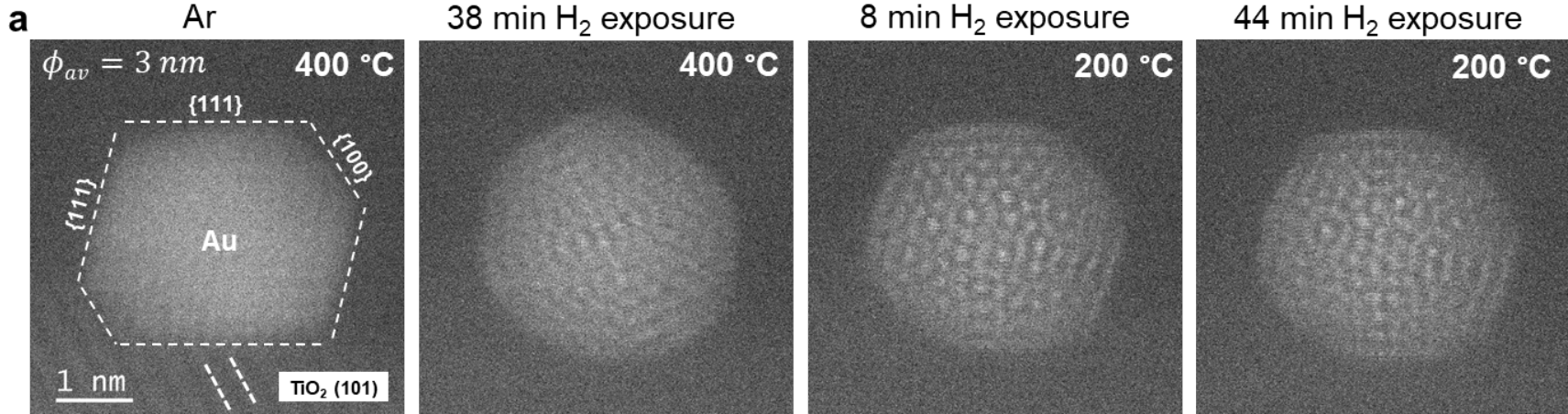


- Both Au NPs maintains their FCC structure under H₂
- Surface restructuration at low-coordinated Au sites

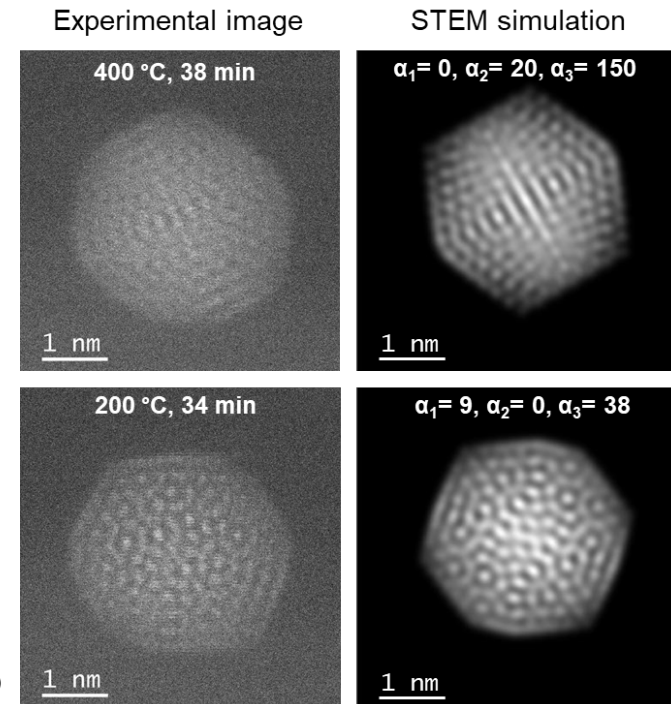


Reactivity of Au NPs of size < 4 nm under H₂

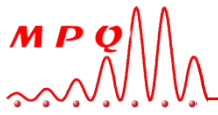
CARMEN Symposium: Evolution



- Structure and shape modification under H₂
- HAADF STEM simulation: icosahedral structure under H₂



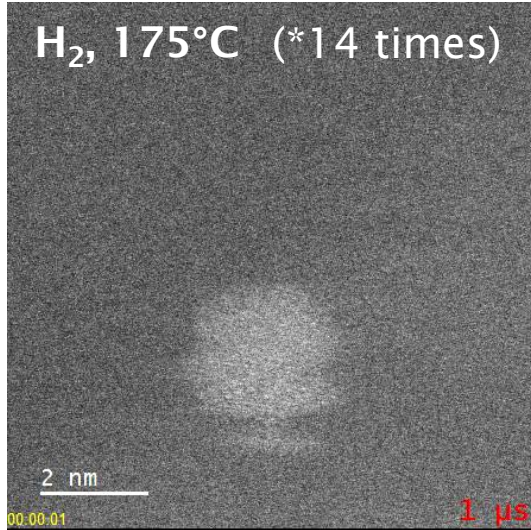
Simulation method described in
(He, D. S. et al. *Micron*. 2015, 74, 47-53)



Reactivity of Au NPs of size < 4 nm under H₂

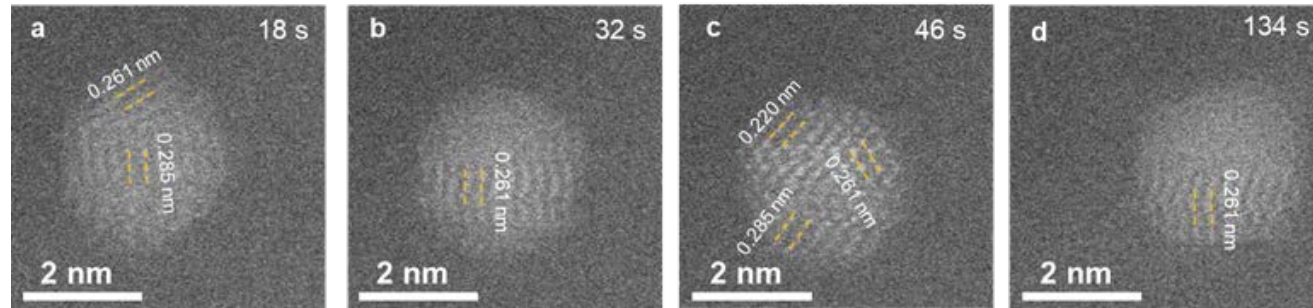
CARMEN Symposium: Evolution

Video recording of Au NP under H₂



HAADF STEM images extracted from a time-lapse video recording

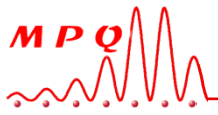
H₂, 175°C



Non FCC structure under H₂

Structural fluctuations of Au NP

Size-dependant reactivity of Au NPs in H₂



Ab Initio Molecular Dynamics study Au NPs of size < 4 nm under H₂

CARMEN Symposium: Evolution

Collaborations

Hazar Guesmi
Qing Wang



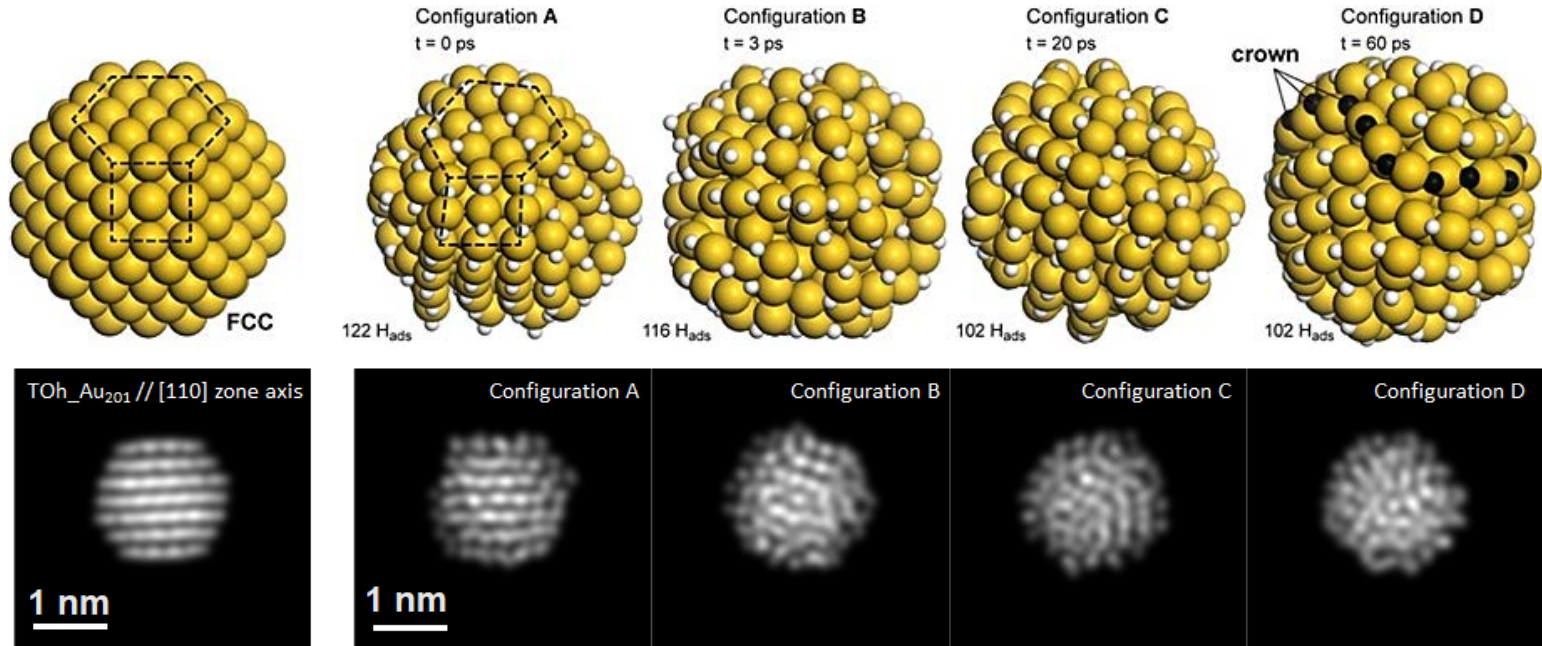
David Loffreda



TOh-Au₂₀₁ (2 nm)

TOh-Au₂₀₁H₁₂₂

AIMD at 500 K

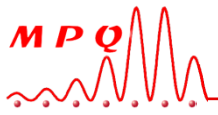


Structure evolution of Toh-Au₂₀₁H₁₂₂ // [110] zone axis during MD simulations

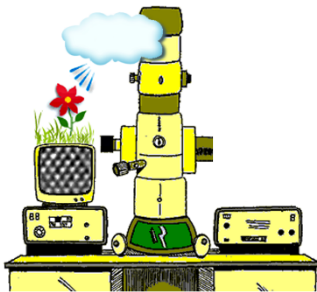
- At 500 K : Transition from FCC to non FCC structure after 60 ps

Strong Au-H interaction :

- Au-H-Au crown lines on the surface
- Highly distorted icosahedral-like core structure consistent with experimental observations

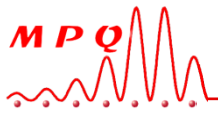


**From nanoscale
in situ observations...**



...to bench-scale synthesis



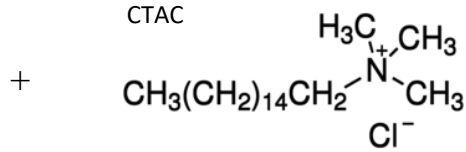


Multi-scale and multi-modal approach

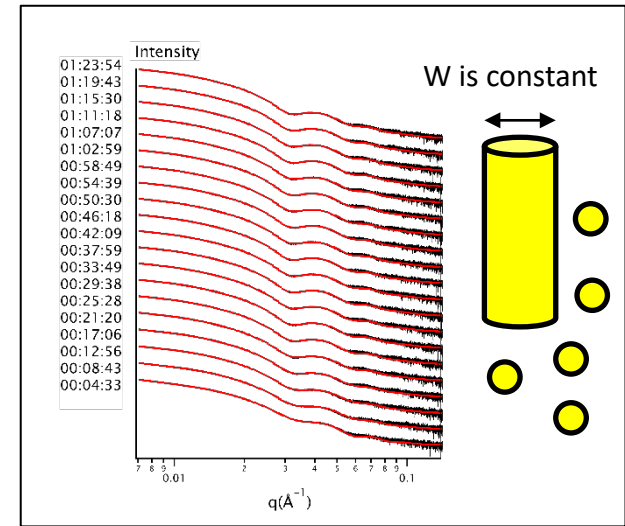
CARMEN Symposium: Evolution

Collaborations

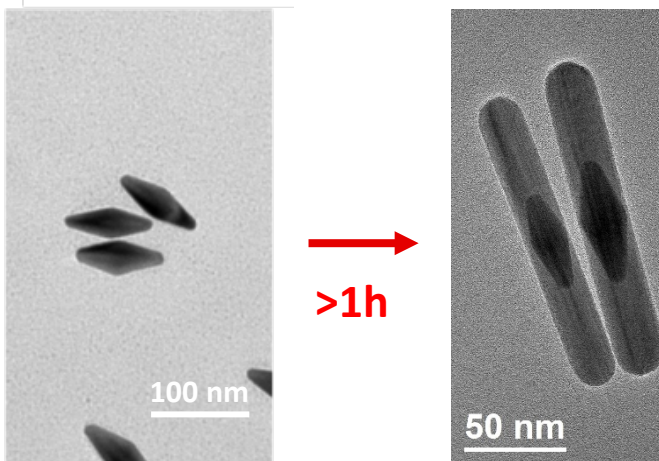
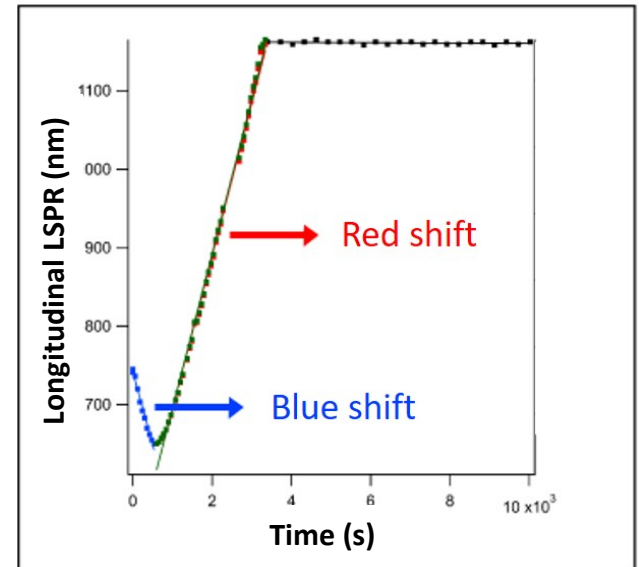
Cyrille Hamon & Doru Constantin

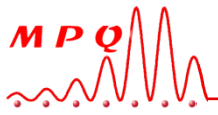


Real-time SAXS (SOLEIL Synchrotron)



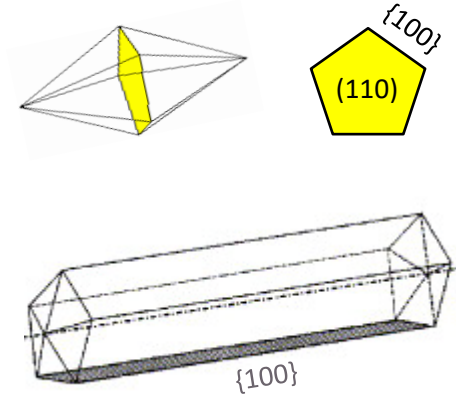
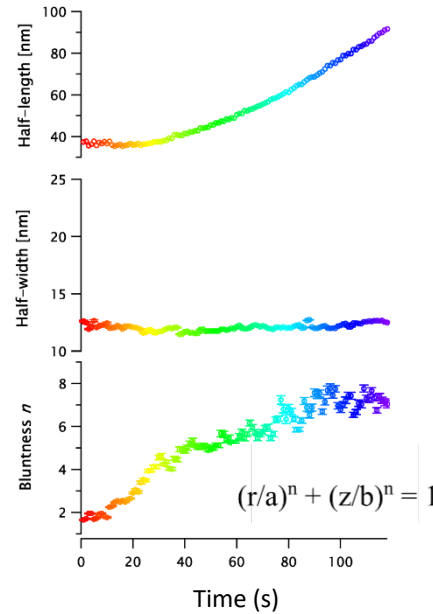
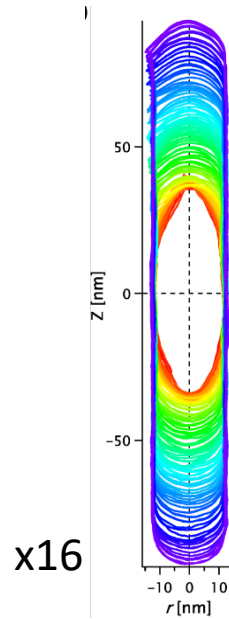
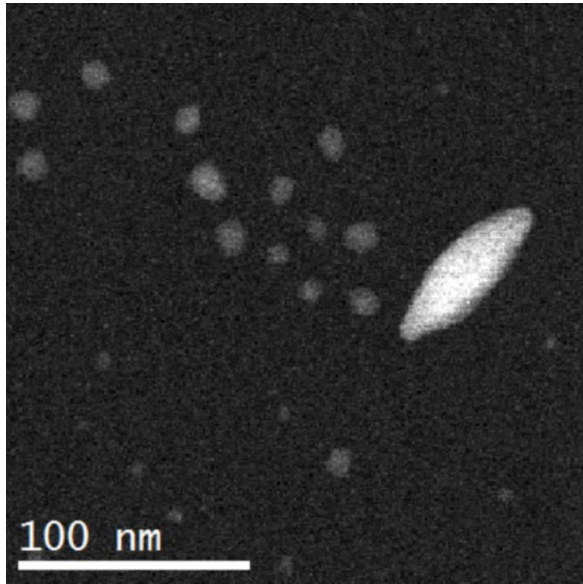
Real-time absorption spectroscopy





Visualize intermediate structures and reaction dynamics

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BEM Simulations of LSPR

$\lambda = 745 \text{ nm}$



$\lambda = 662 \text{ nm}$



$\lambda = 646 \text{ nm}$

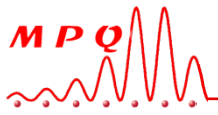


$\lambda = 721 \text{ nm}$



$\lambda = 794 \text{ nm}$

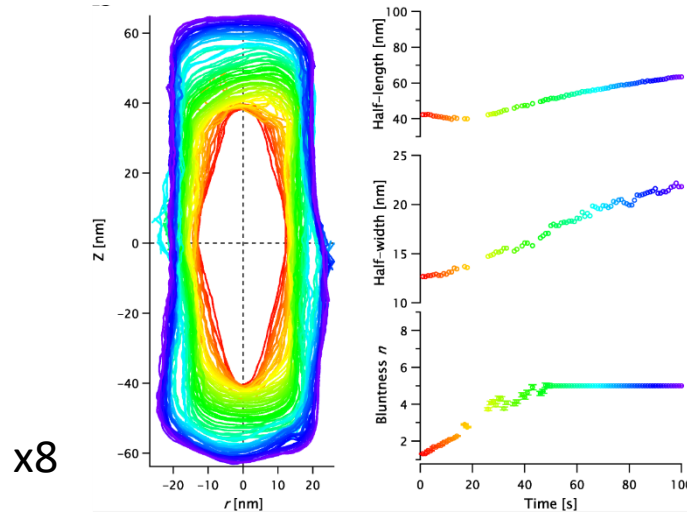
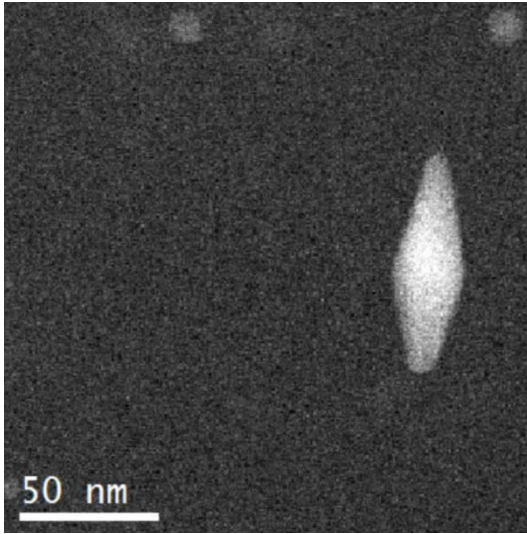




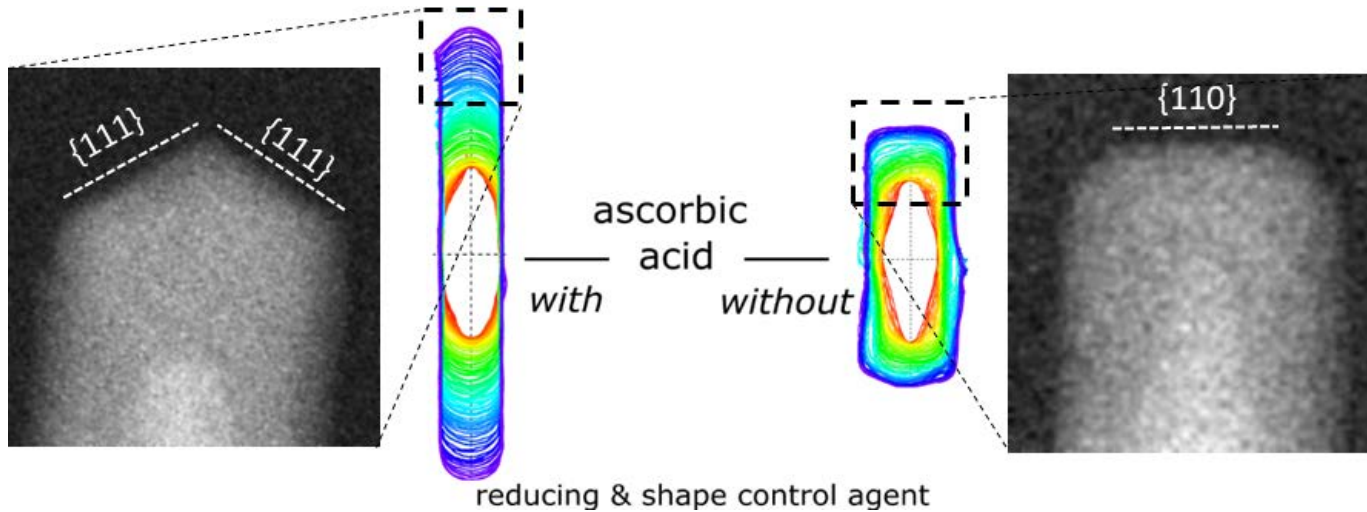
Reveal the role of each chemical in the synthesis

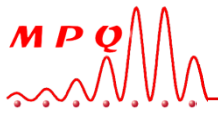
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Without ascorbic acid

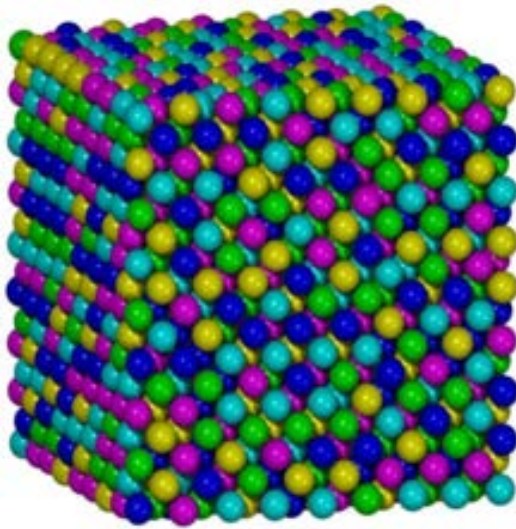


Ascorbic acid is not only a source of electron but it is also shape directing agent !





Bulk HEA



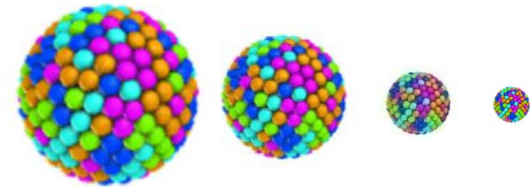
Mechanical properties

and also **catalytic, H storage, anti-corrosion** applications

Four core effects:

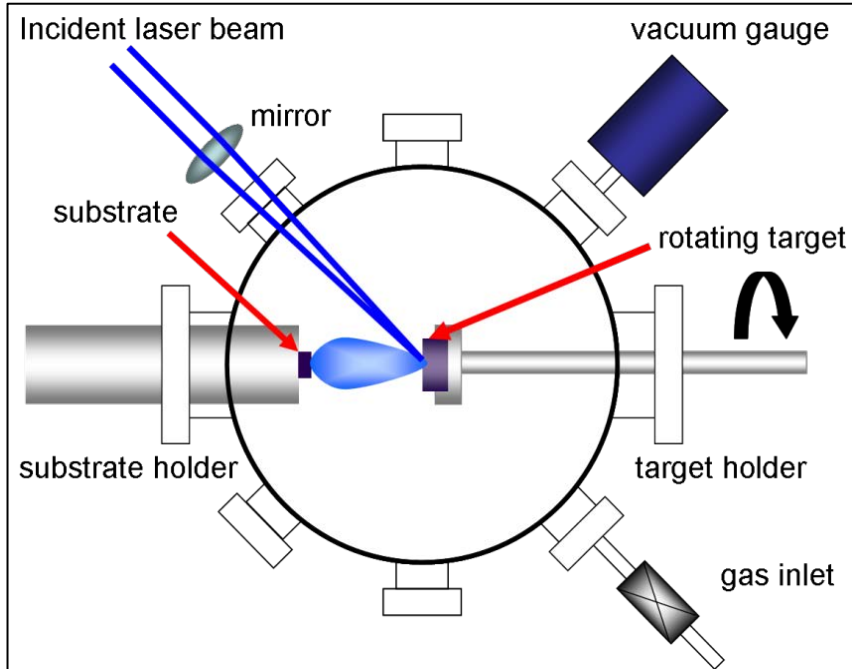
1. Configurational entropy
2. Sluggish diffusion
3. Lattice distortion
4. Cocktail effect

HEA Nanoparticles

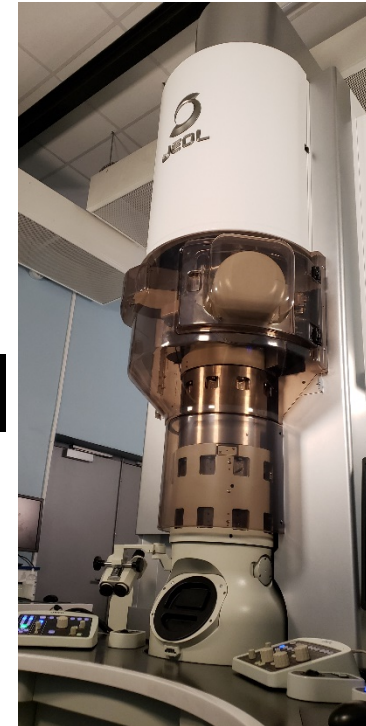
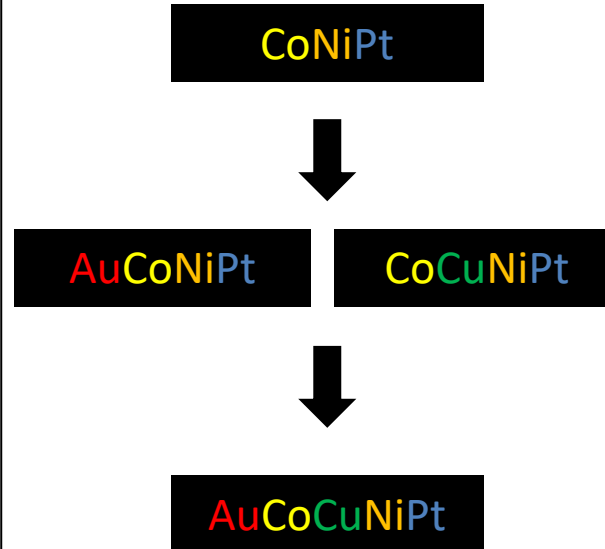


What about size effects ?

Carbothermal shock synthesis of HEA NPs,
Y. Yao, et al , Science 359, 1489 (2018)



Size < 10 nm



High control over the size and composition of bimetallic NPs
 (quantity of deposited materials, deposition rate,
 sequence, temperature...)

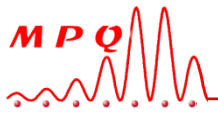
CoPt: Nature materials 8, 940 (2009)

AuCu: Physical Chemistry Chemical Physics 17, 28339 (2015)

AuPd: Nanoscale 6, 10423-10430 (2014)

CuAg: Faraday discussions 138, 375 (2008)

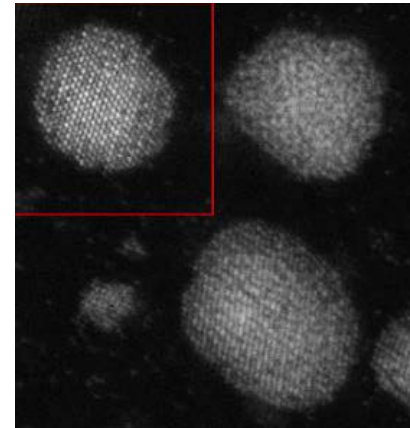
- Double-corrected
- Centurio Large-angle EDS
- 4D-STEM
- Cold FEG (0.3 eV)
- One view camera
- GIF Quantum ER
- Tomography
- In situ TEM holders



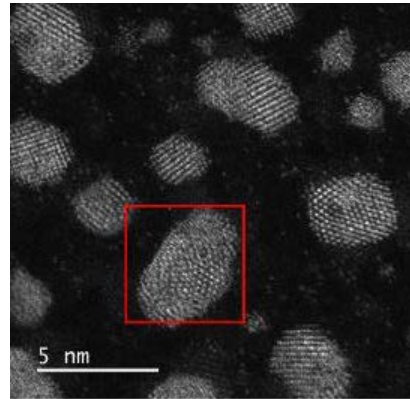
Structural properties of HEA NPs fabricated by PLD

FCC structure with more defects in quaternary and quinary nano-HEA

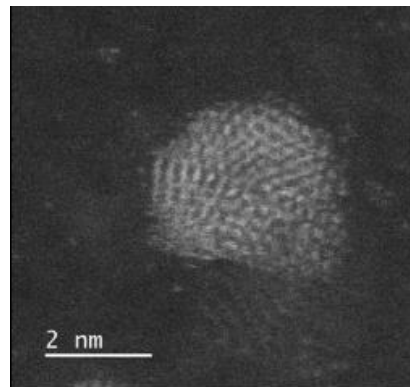
CoNiPt



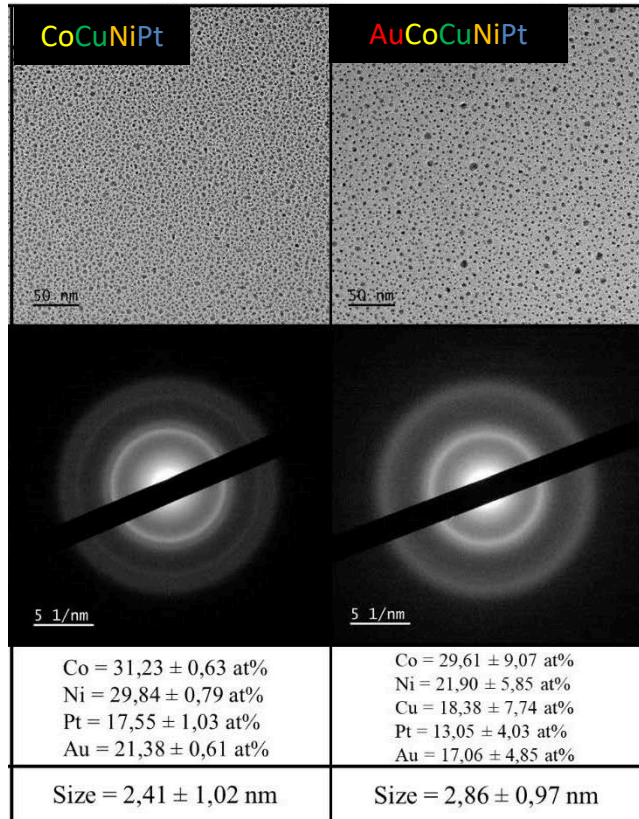
CoNiPt



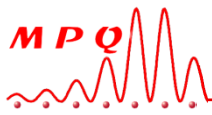
CoCuNiPt



AuCoCuNiPt



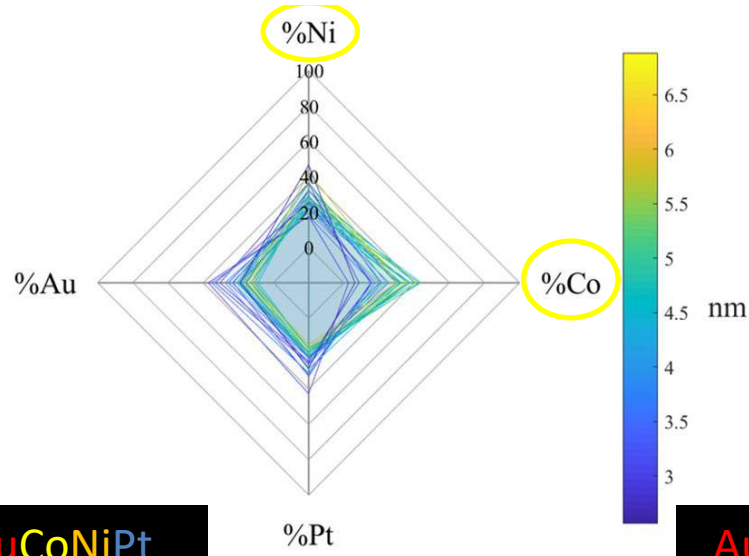
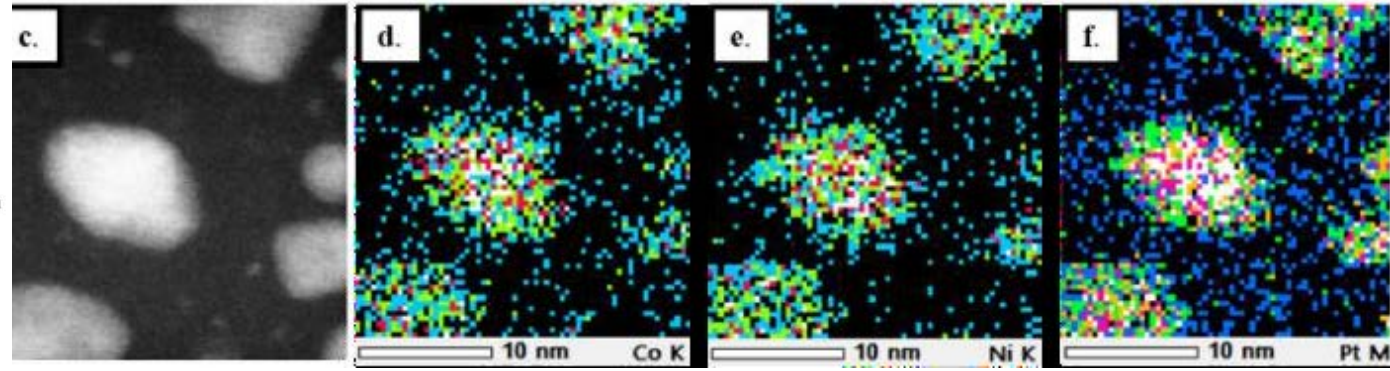
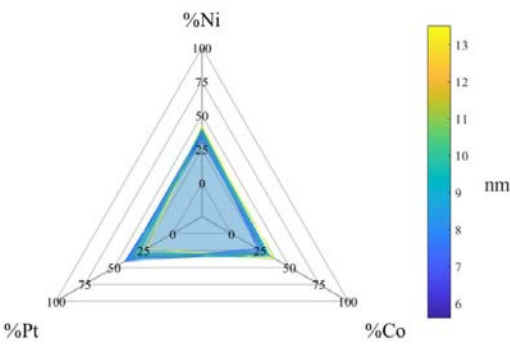
Synthesis at 600°C



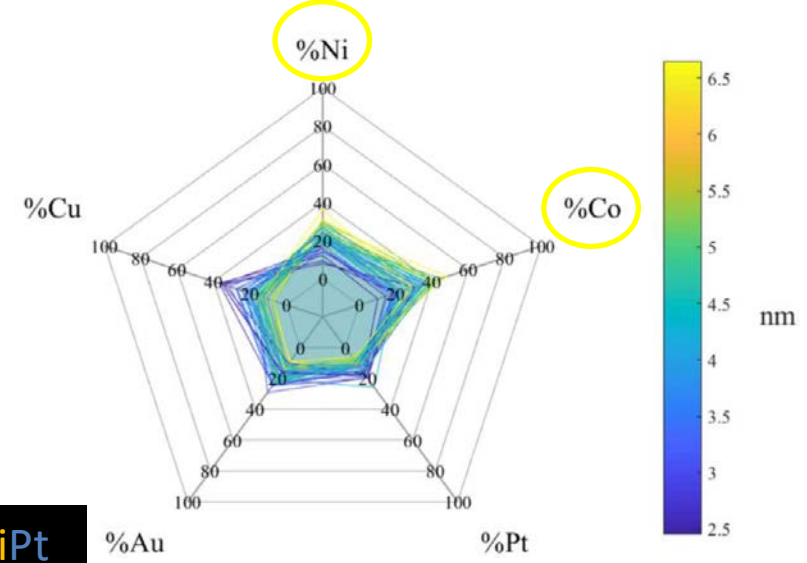
Structural properties of HEA NPs fabricated by PLD

CoNiPt

Chemical mapping and composition at the single NP level



AuCoNiPt



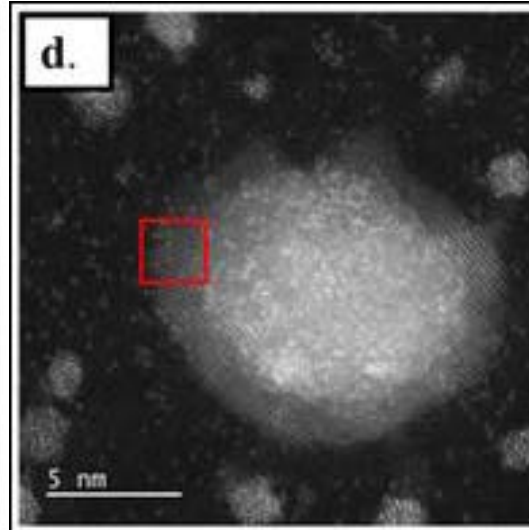
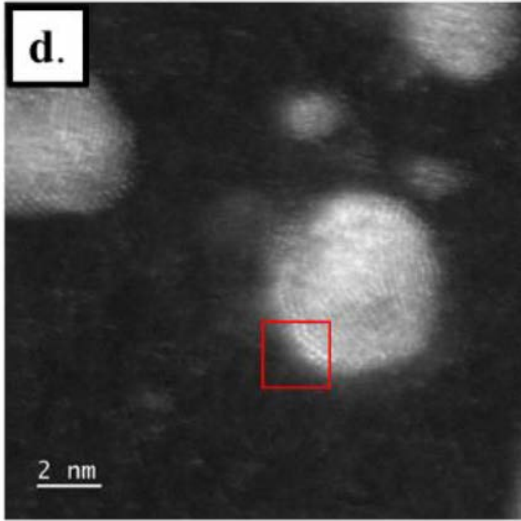
AuCoCuNiPt

	All NPs	NPs with size < 5 nm	NPs with size > 5 nm
at% of Co	28.16 ± 11.53	25.69	35.58 ++
at% of Ni	29.01 ± 6.95	28.00	32.04 ++
at% of Pt	23.10 ± 6.14	24.87	17.79 --
at% of Au	19.72 ± 7.42	21.43	14.59 --

	All NPs	NPs with size < 4 nm	NPs with size > 4 nm
at% of Co	29.61 ± 9.07	23.86	33.91 ++
at% of Ni	21.90 ± 5.85	17.71	24.79 ++
at% of Cu	18.38 ± 7.74	24.04	14.26 --
at% of Pt	13.05 ± 4.03	15.57	11.33 --
at% of Au	17.06 ± 4.85	18.82	15.72 --

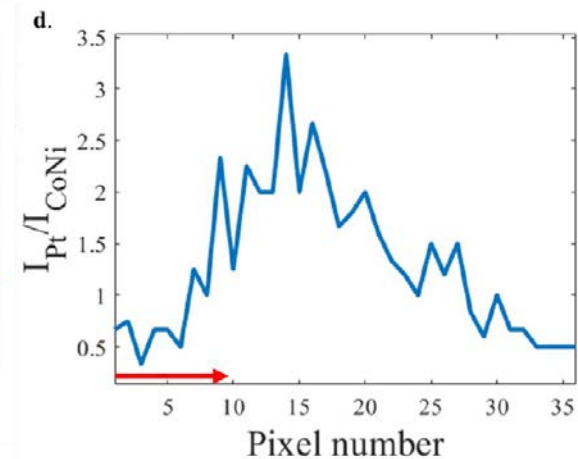
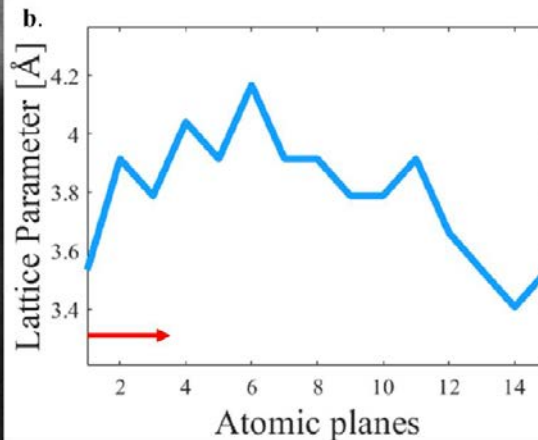
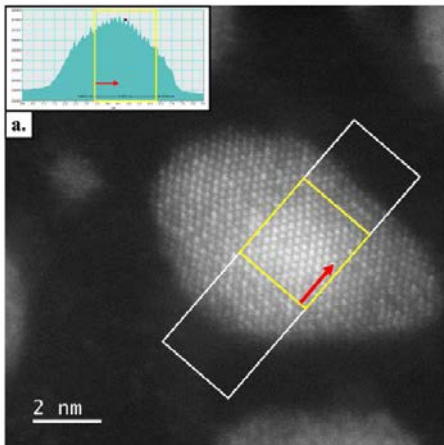
CoCuNiPt

AuCoCuNiPt

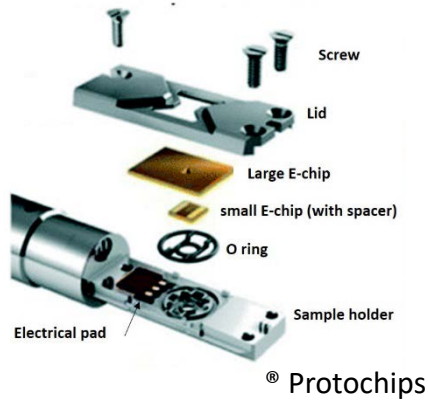


Deviating from the equiatomic composition induces phase separation

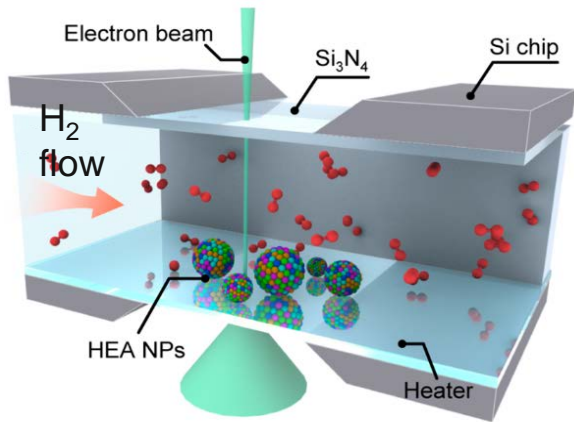
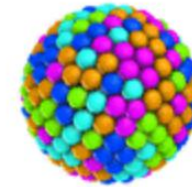
Co₂₈Ni₂₈Pt₄₅

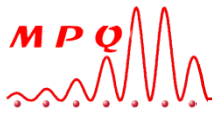


Evaluating the potential of HEA NPs for H storage and modeling



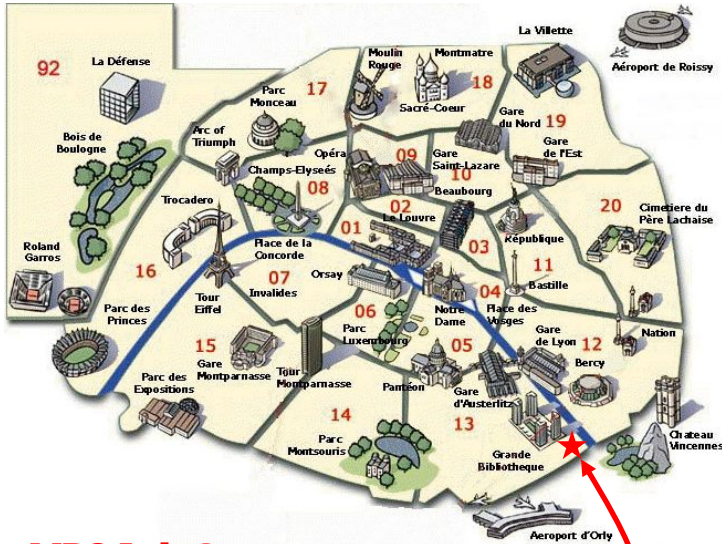
Atomic potentials for ternary CoPtNi alloys under development (LEM + CiNAM)





National TEM user facility

CARMEN Symposium: Evolution

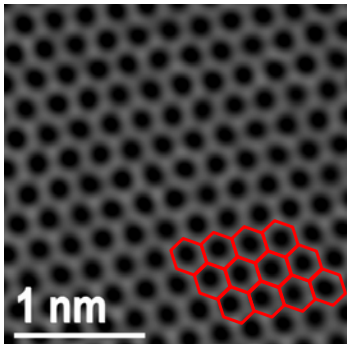


**MPQ Lab @
University of Paris Cité**

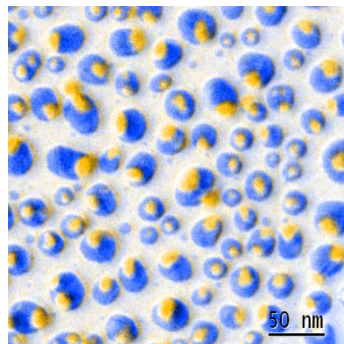


- Double-corrected
- Centurio Large-angle EDS
- 4D-STEM
- Cold FEG (0.3 eV)
- One view camera
- GIF Quantum ER
- Tomography
- In situ TEM holders

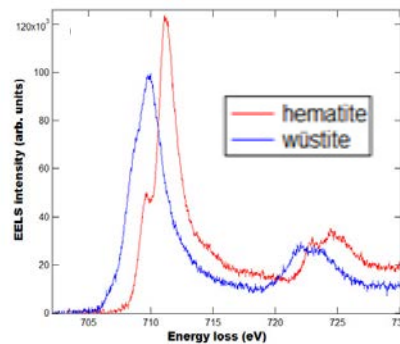
Sub-Angstrom imaging



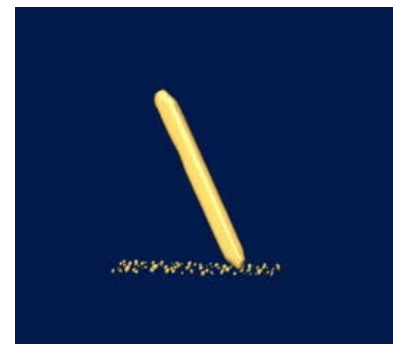
Chemical mapping



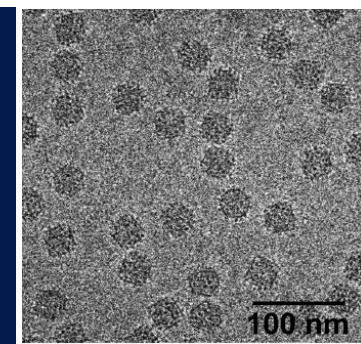
EELS spectroscopy

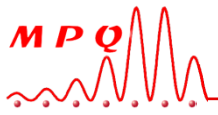


3D Imaging



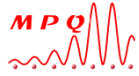
Cryo TEM





Thank you

CARMEN Symposium: Evolution



Jaysen Nelayah
Christian Ricolleau
Guillaume Wang
Chisato Takahashi
Nathaly Ortiz Pena
Abdelali Khelfa
Abdallah Nassereddine
Gregoire Breyton



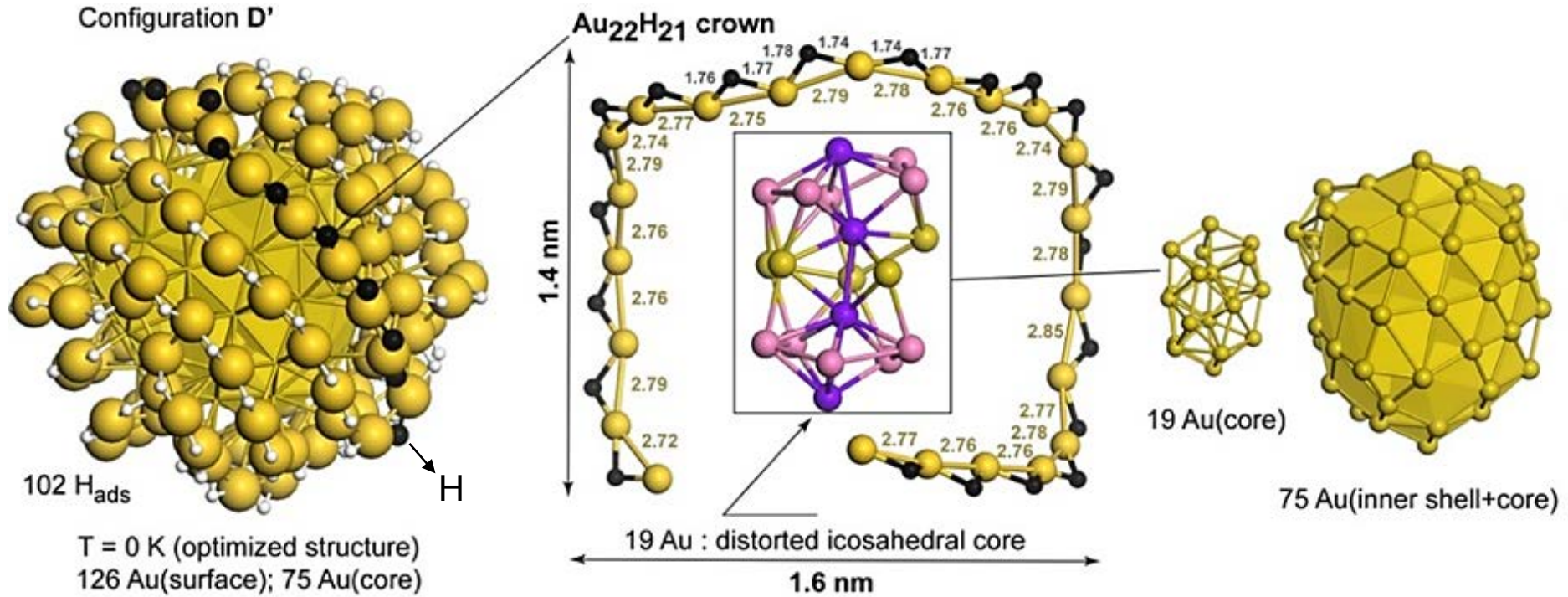
Hakim Amara
Yann Lebouar



Cyrille Hamon
Daru Constantin
Kinanti Aliyah

Foundings :





Strong Au-H interaction :

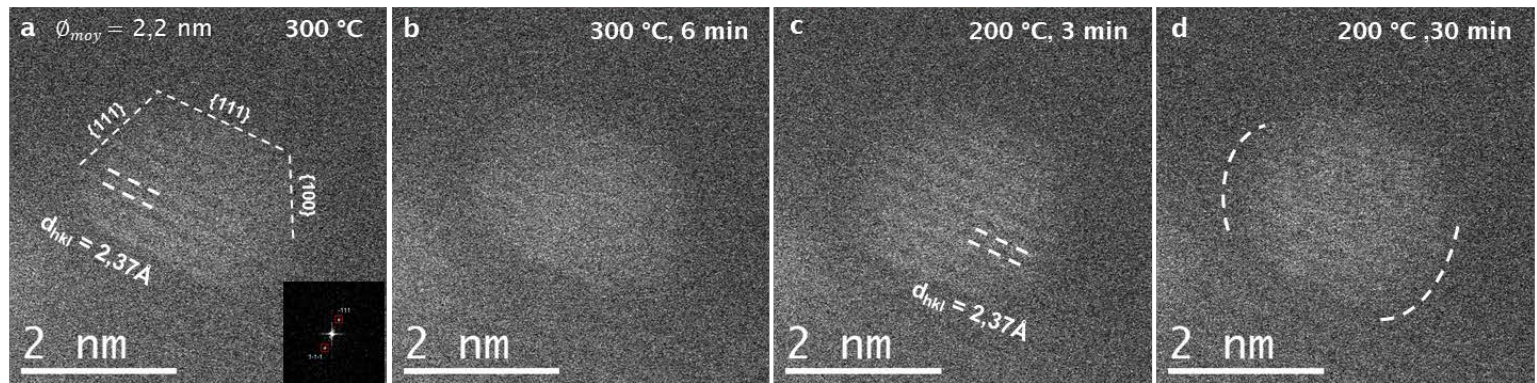
- Au-H-Au crown lines on the surface
- Highly distorted icosahedral-like core structure → consistent with experimental observations

Reactivity of Au NPs under static butadiene (C_4H_6) environment

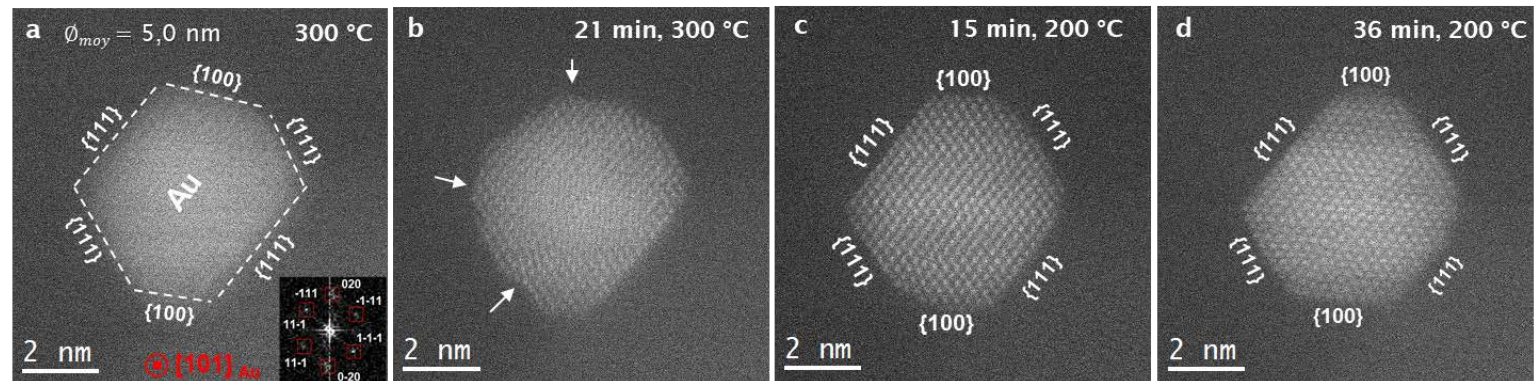
(a) : 40 Pa Ar

(b-d) : 10^5 Pa (0,46% C_4H_6/He)

Au < 4nm



Au > 4nm

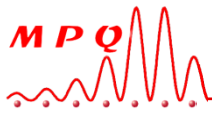


- Stable FCC structure
- Morphological change : interaction with C_4H_6

Au < 4nm : adsorption on low coordinated atoms

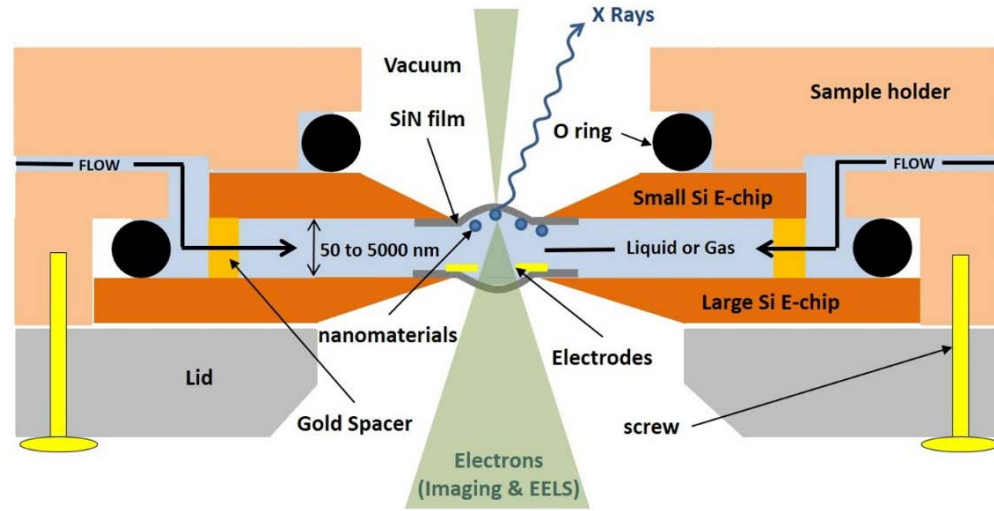
Au > 4nm

300°C : adsorption on low coordinated atoms
200°C : adsorption on {111} and {100} surface



Highlight the interdisciplinary potential of liquid-cell TEM

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- ® Protochips

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