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)

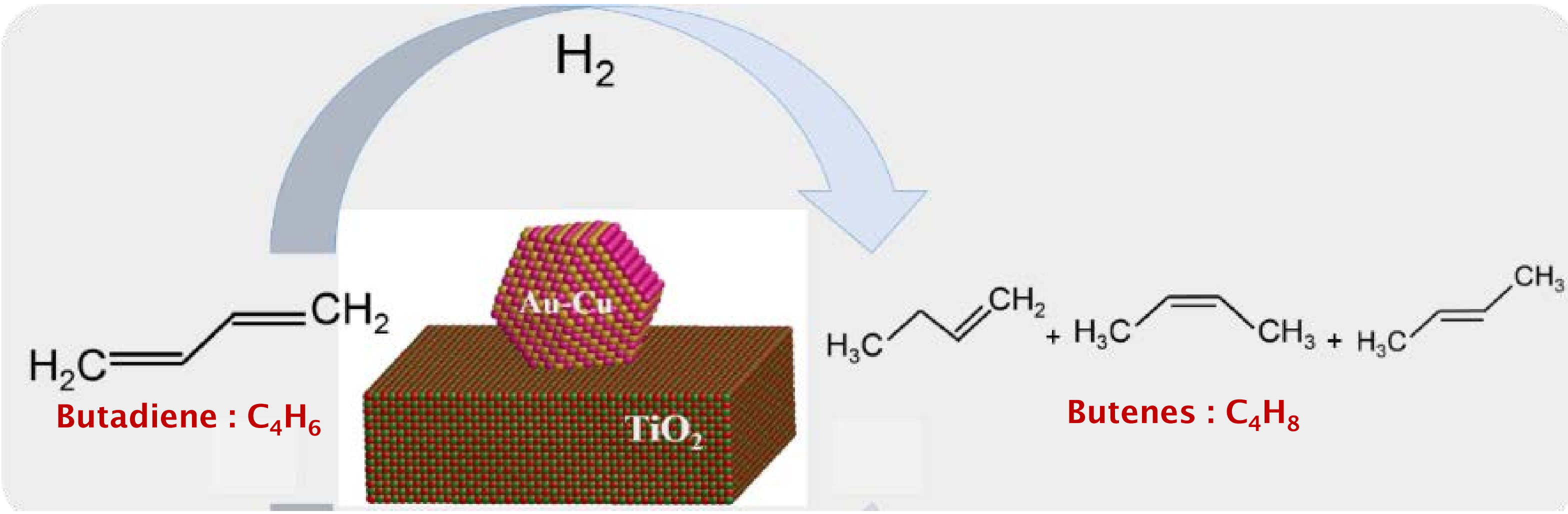
Content

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

Selective hydrogenation of butadiene by Au/TiO_2 catalysts

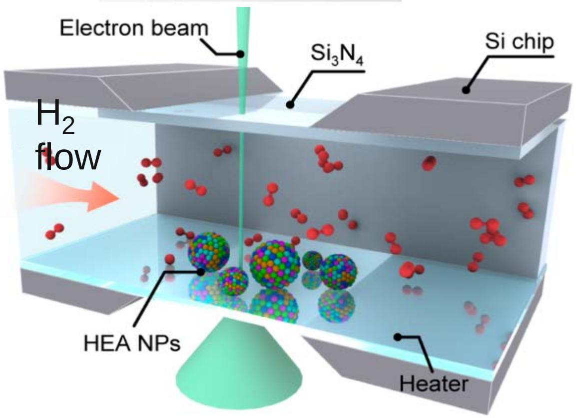


Gain fundamental real time atomic-scale insights into the interplay between structure and catalytic properties of heterogeneous catalysts by *operando* transmission electron microscopy (TEM)

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

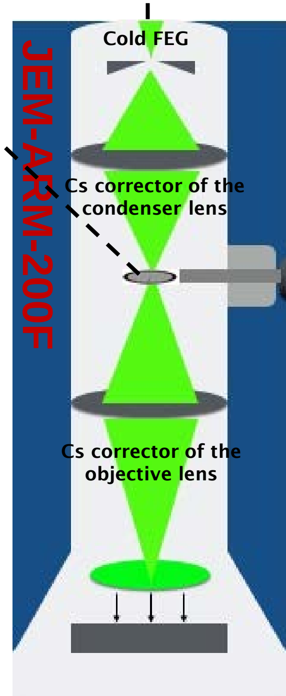
Protochips Atmosphere™
TEM environmental high-pressure gas cell

Planar (vertical) nanoreactor



- *In situ* temp : up to 1200 °C
- Pressure: up to 1 atm
- m_{cat} = ~ng
- V_{gas} = ~ μl

Super TEM 2



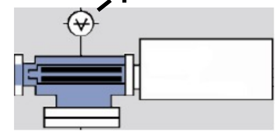
Holder

Outlet

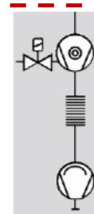
Inlet

Residual gas analyzer (RGA ,PrismaPro)

High precision valve (UDV 40)



Mass spectrometer

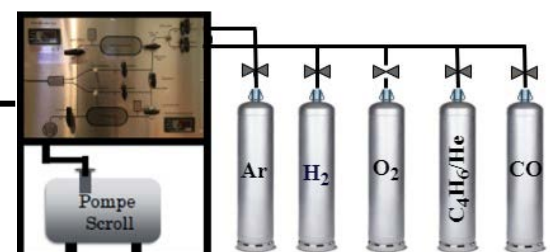


Turbopump (HiPace 80)

Diaphragm pump (MVP 040-2)

Elimination of mechanical vibration induced by the turbomolecular pump

Manual gas distributor

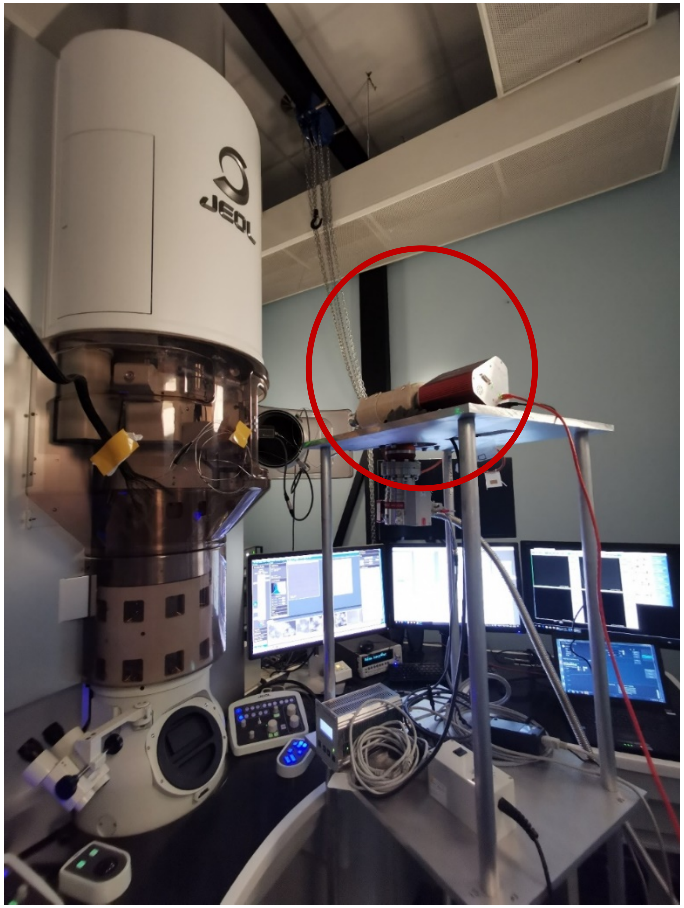


Challenge :

Achieve a high sensitivity for trace gas detection

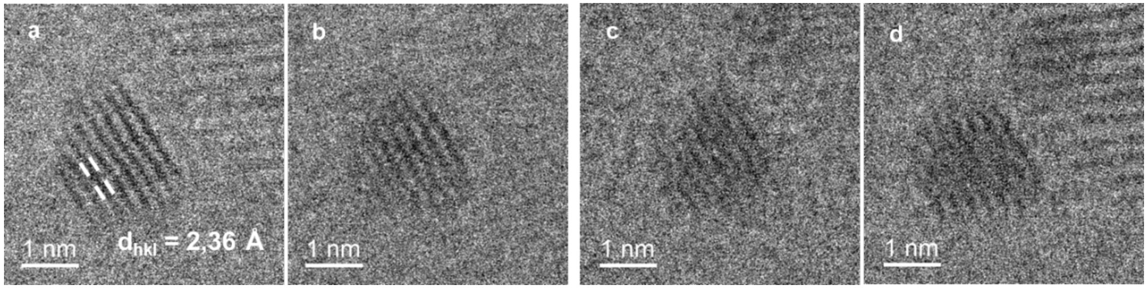
Keep the atomic resolution of Super TEM

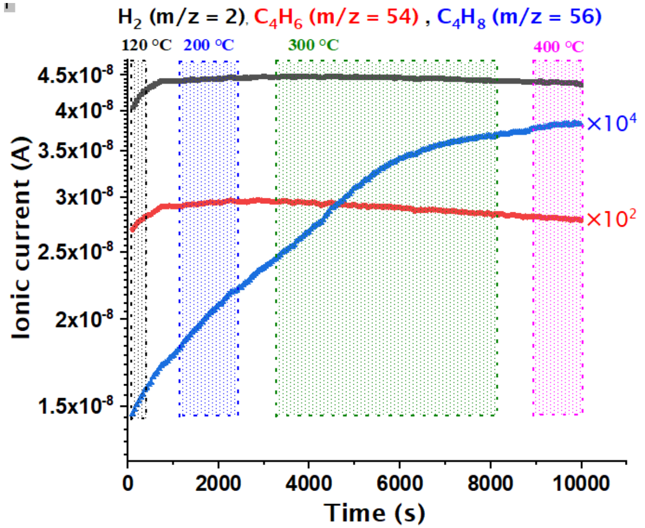
Operational operando TEM plateform at MPQ



<u>PrismaPro® by PFEIFFER</u>
Mass range: **1-100 amu**
Detector : Faraday/ C-SEM
Operating pressure max : **$5\cdot10^{-4}$ mbar**
Detection limit min : **$4\cdot10^{-13}$ mbar**

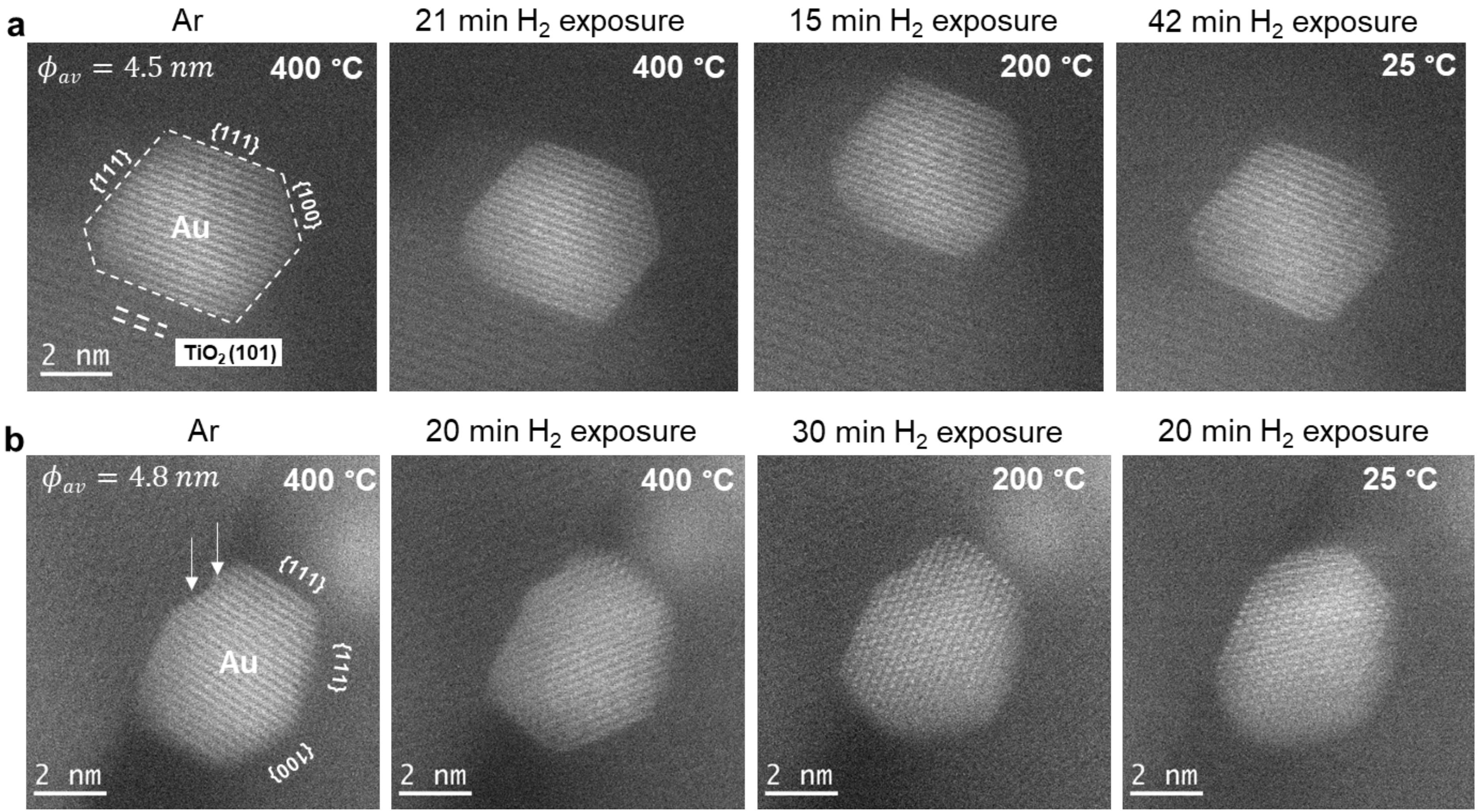
Au NP in butadiene hydrogenation reaction





Reactivity of Au NPs of size > 4 nm under H_2

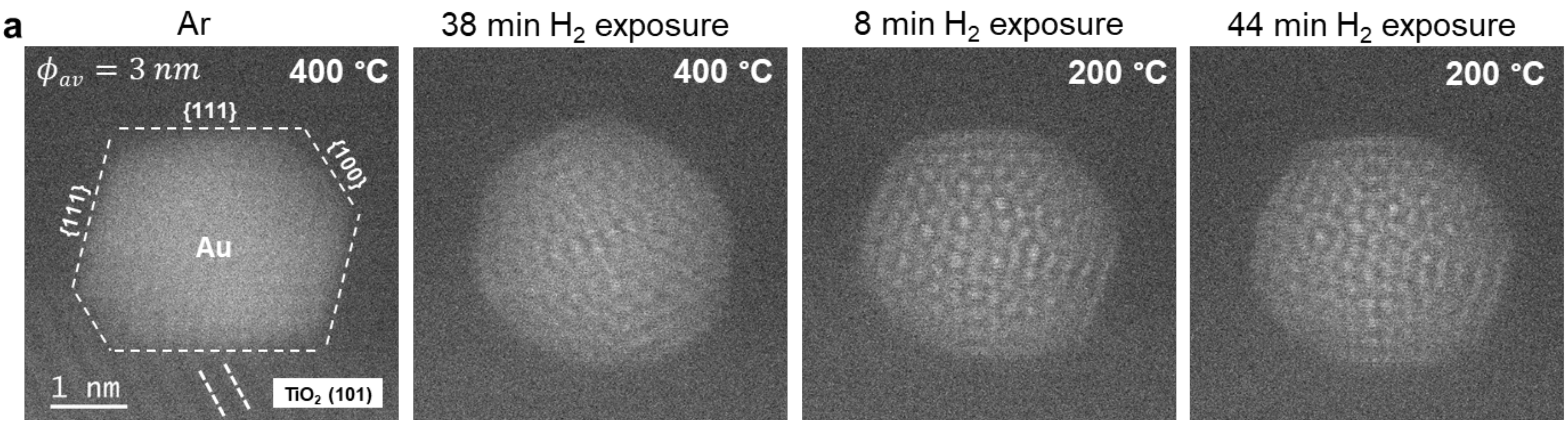
Atm pressure : Static H_2 environment



- Both Au NPs maintains their FCC structure under H_2
- Surface restructuration at low-coordinated Au sites

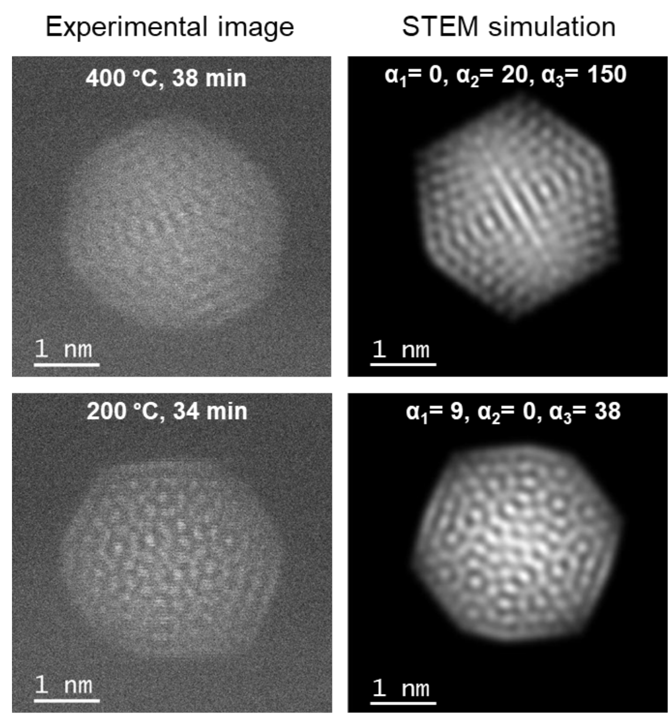
Nassereddine, Abdallah, Qing Wang, David Loffreda, Christian Ricolleau, Damien Alloyeau, Catherine Louis, Laurent Delannoy, Jaysen Nelayah, and Hazar Guesmi. Small (2021).

Reactivity of Au NPs of size < 4 nm under H_2



- Structure and shape modification under H_2

- HAADF STEM simulation: icosahedral structure under H_2



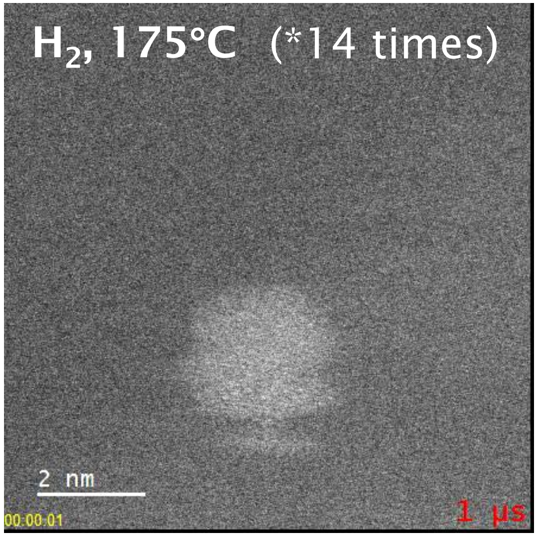
Simulation method describied in

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

Nassereddine, Abdallah, Qing Wang, David Loffreda, Christian Ricolleau, Damien Alloyeau, Catherine Louis, Laurent Delannoy, Jaysen Nelayah, and Hazar Guesmi. Small (2021).

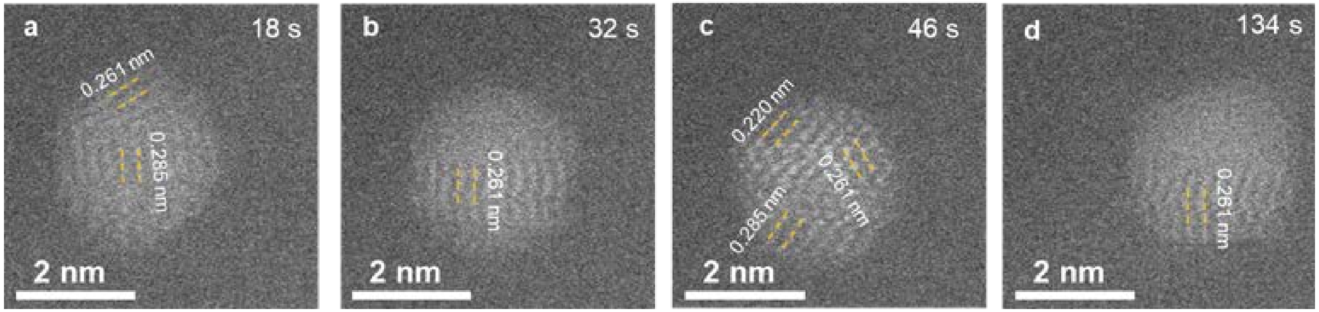
Reactivity of Au NPs of size < 4 nm under H_2

Video recording of Au NP under H_2



HAADF STEM images extracted from a time-lapse video recording

H_2, 175°C



Non FCC structure under H_2

Structural fluctuations of Au NP

Size-dependant reactivity of Au NPs in H_2

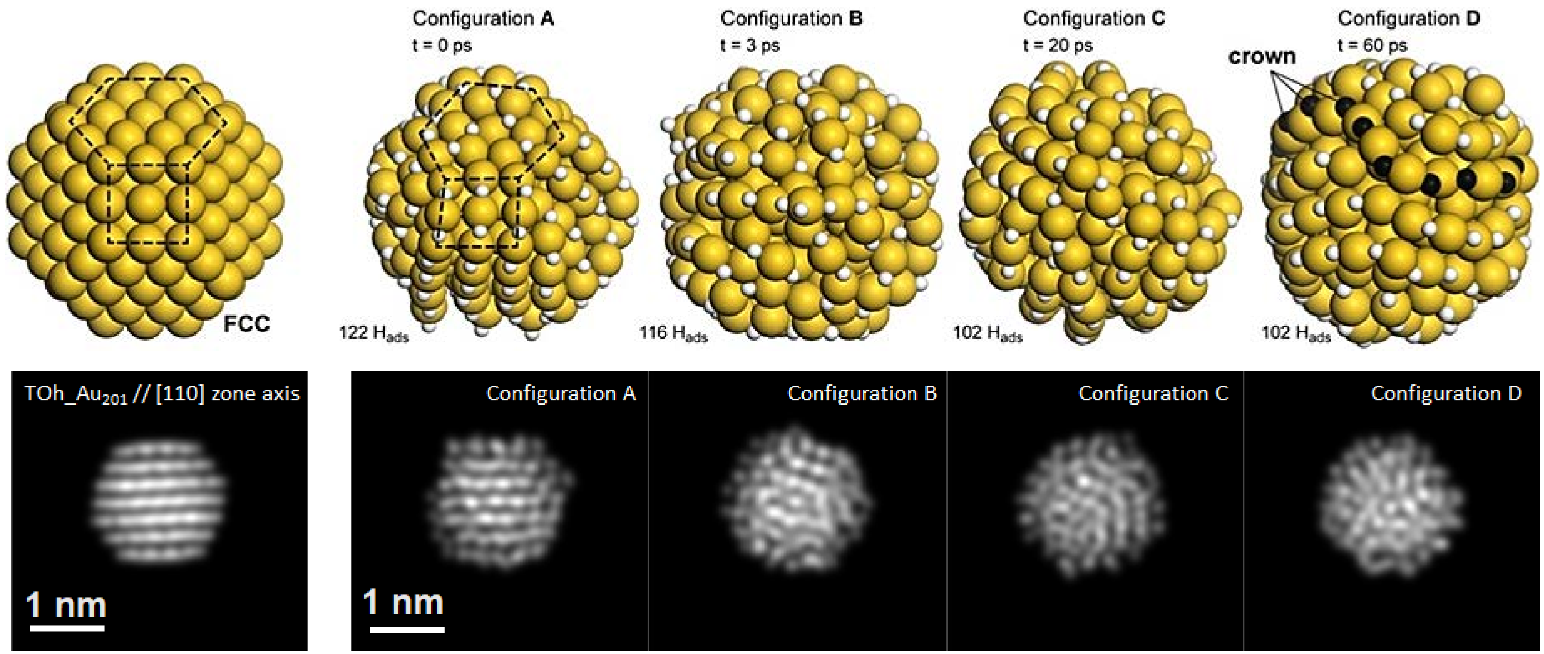
Ab Initio Molecular Dynamics study Au NPs of size < 4 nm under H_2

Collaborations

Hazar Guesmi
Qing Wang
iCGM Institut Charles Gerhardt Montpellier

David Loffreda
Laboratoire de Chimie ENS de Lyon

TOh-Au_{201} (2 nm) | TOh-$Au_{201}H_{122}$ | AIMD at 500 K



Structure evolution of Toh-$Au_{201}H_{122}$ // [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

Nassereddine Abdallah, Qing Wang, David Loffreda, Christian Ricolleau, Damien Alloyeau, Catherine Louis, Laurent Delannoy, Jaysen Nelayah, and Hazar Guesmi. Small (2021).

TEM in liquid medium: understanding gowth by chemistry

From nanoscale
in situ observations…

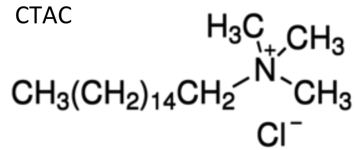
…to bench-scale synthesis

Multi-scale and multi-modal approach

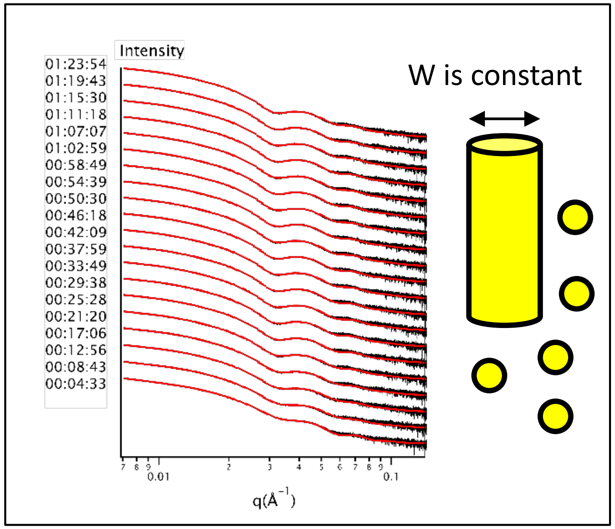
Collaborations Cyrille Hamon & Doru Constantin

+

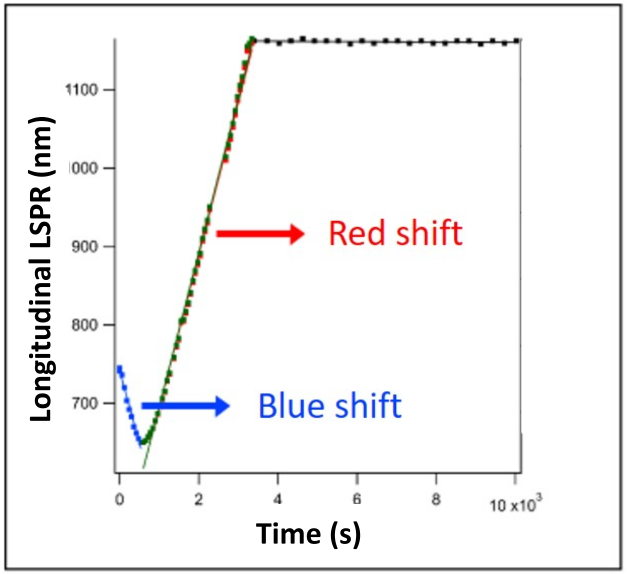
CTAC

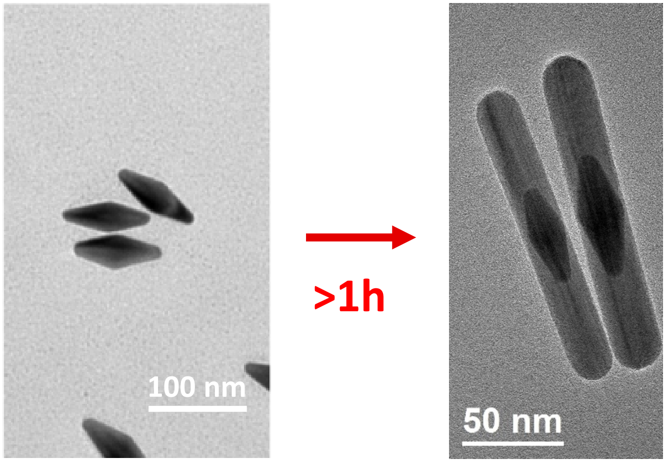


Real-time SAXS (SOLEIL Synchrotron)

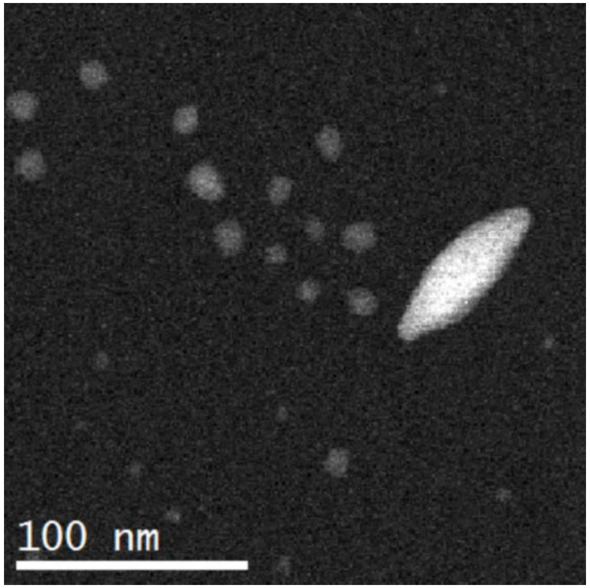


Real-time absorption spectroscopy

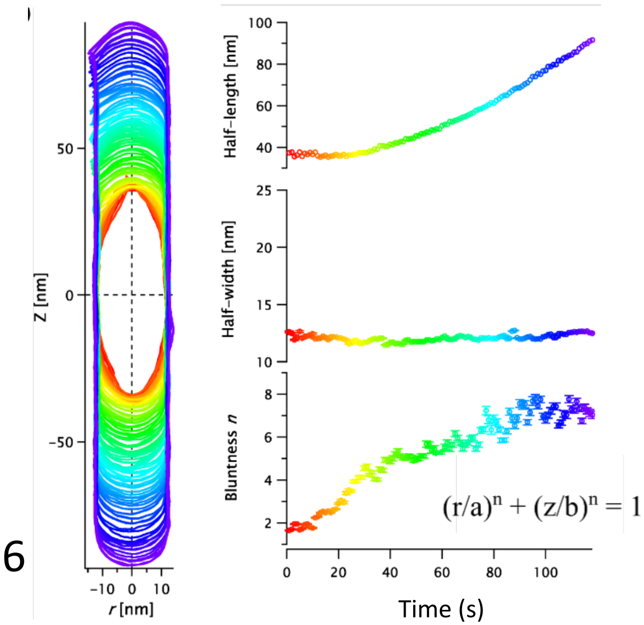


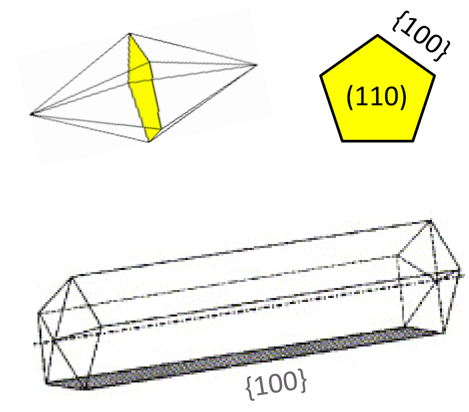


Visualize intermediate structures and reaction dynamics

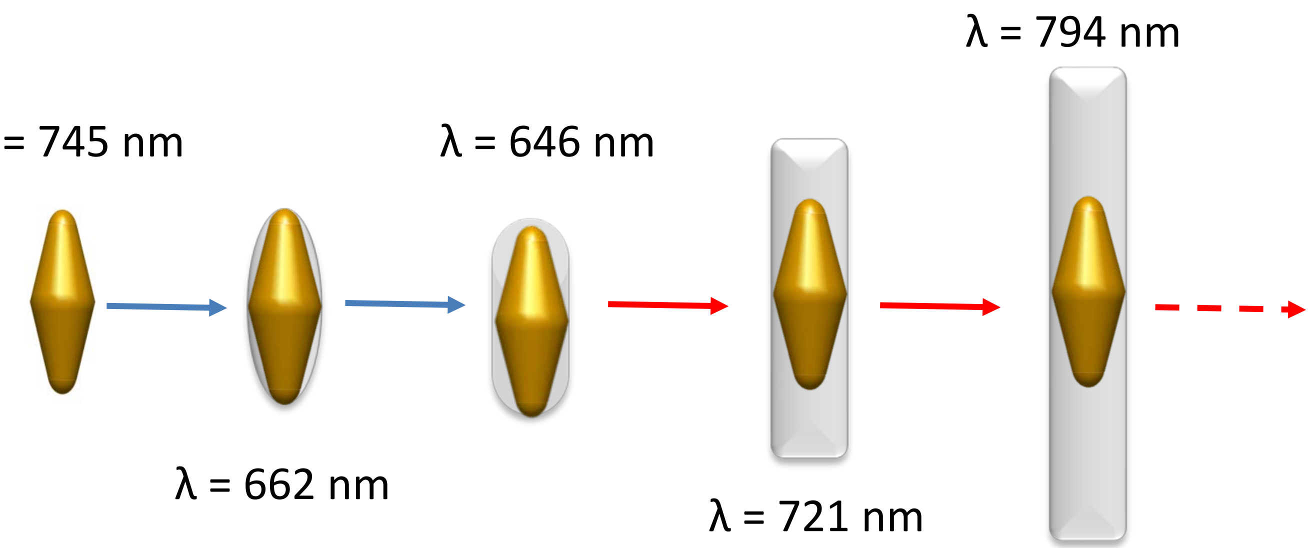


x16





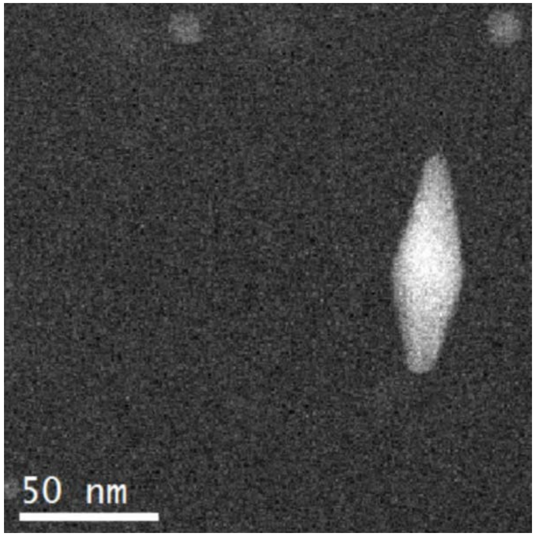
BEM Simulations of LSPR



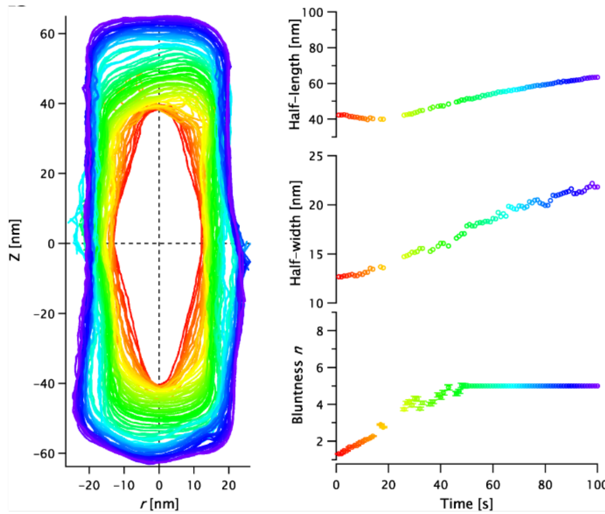
Aliyah et al. J. Phys. Chem. Lett. 11 2830 (2020)

Reveal the role of each chemical in the synthesis

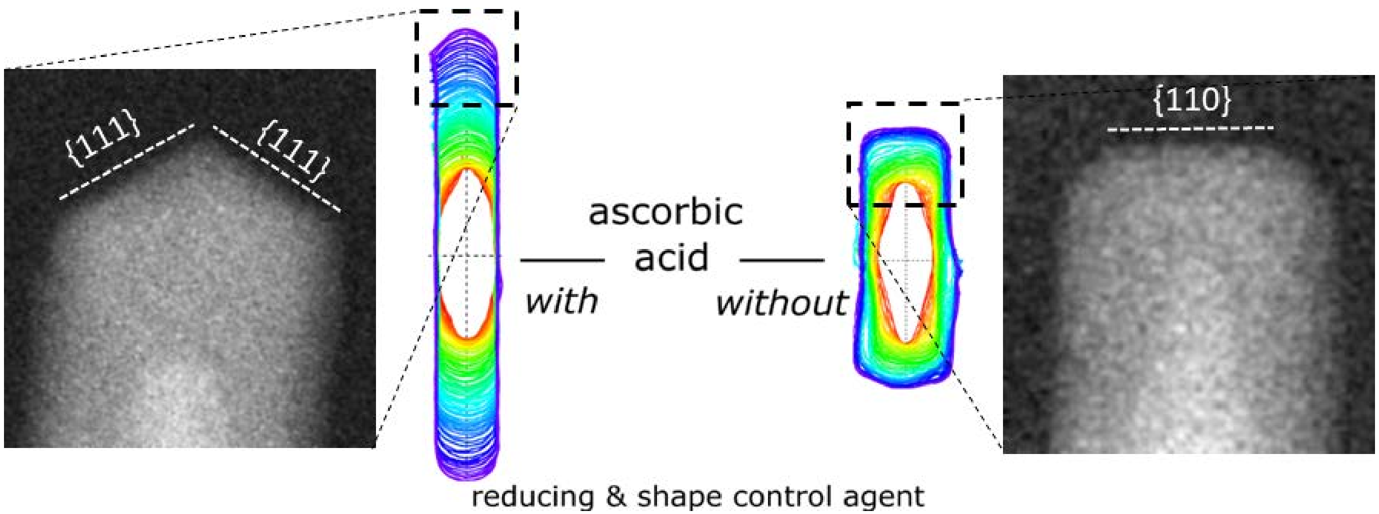
Without ascorbic acid



x8

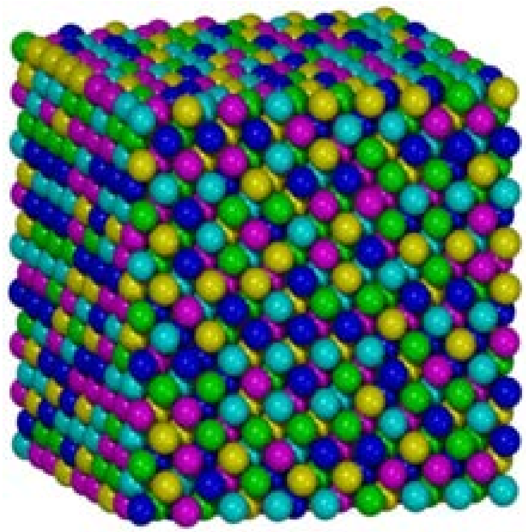


Ascorbic acid is not only a source of electron but it is also shape directing agent !



Aliyah et al. J. Phys. Chem. Lett. 11 2830 (2020)

Bulk HEA



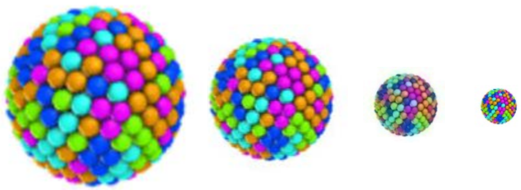
Mechanical properties

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

Four core effects:

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

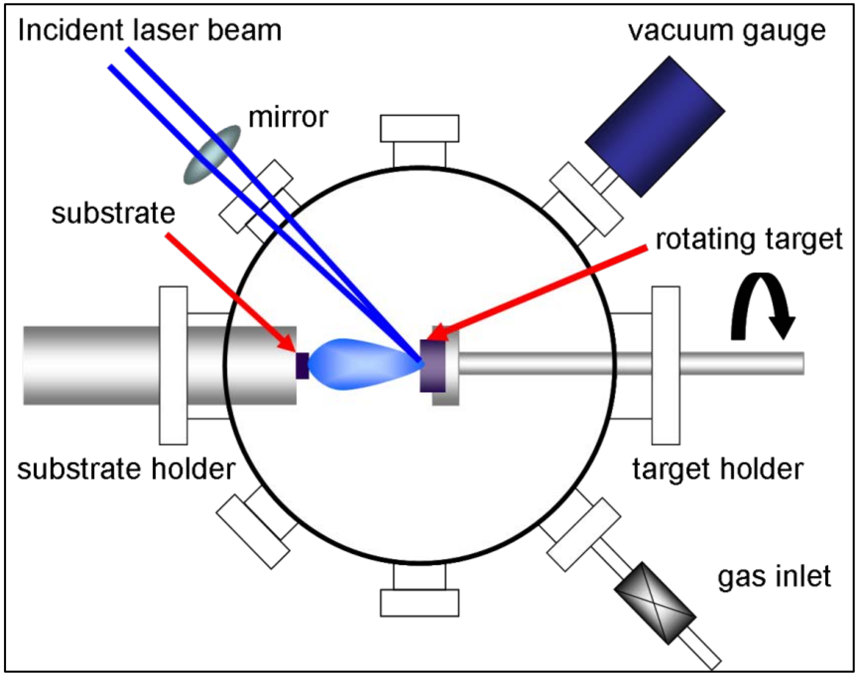
HEA Nanoparticles



What about size effects ?

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

Synthesis of HEA NPs by PLD

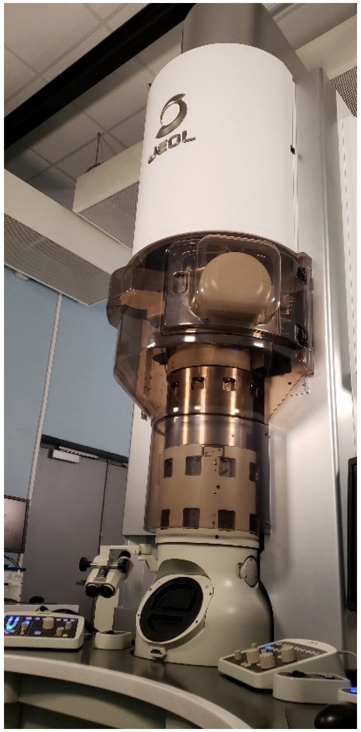


Size < 10 nm

CoNiPt

AuCoNiPt | CoCuNiPt

AuCoCuNiPt



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)

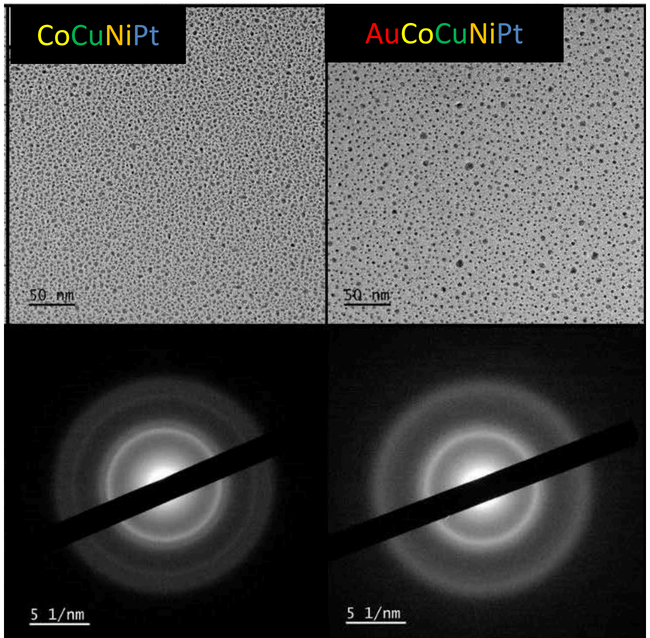
- **Double-corrected**
- **Centurio Large-angle EDS**
- **4D-STEM**
- **Cold FEG (0.3 eV)**
- **One view camera**
- **GIF Quantum ER**
- **Tomography**
- **In situ TEM holders**

metsa

Structural properties of HEA NPs fabricated by PLD

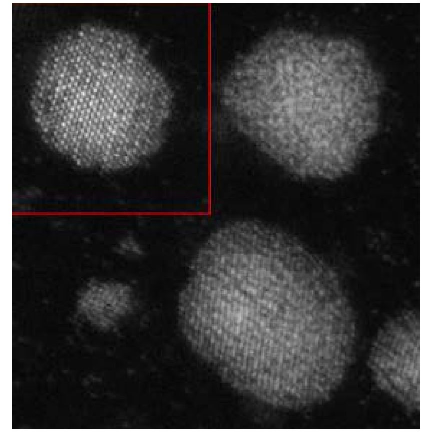
FCC structure with more defects in quaternary and quinternary nano-HEA

CoNiPt

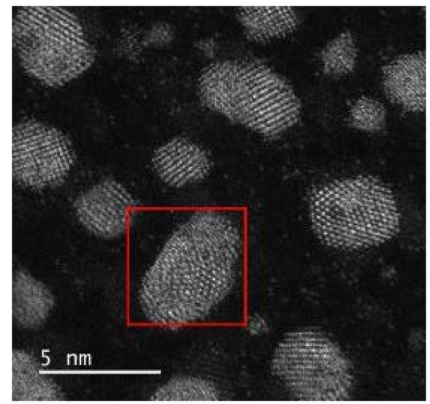


Co = 31,23 ± 0,63 at% Ni = 29,84 ± 0,79 at% Pt = 17,55 ± 1,03 at% Au = 21,38 ± 0,61 at%	Co = 29,61 ± 9,07 at% Ni = 21,90 ± 5,85 at% Cu = 18,38 ± 7,74 at% Pt = 13,05 ± 4,03 at% Au = 17,06 ± 4,85 at%
Size = 2,41 ± 1,02 nm	Size = 2,86 ± 0,97 nm

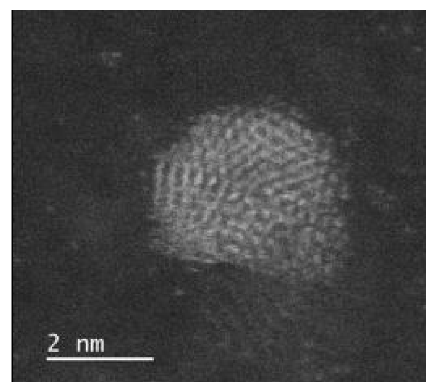
Synthesis at 600°C



CoNiPt



CoCuNiPt

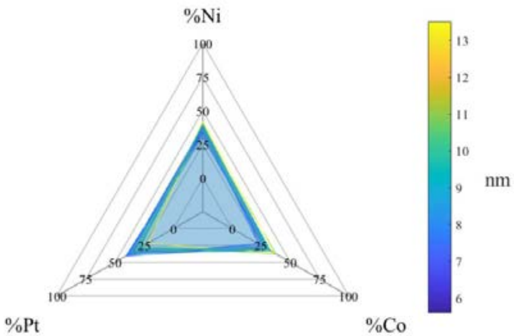


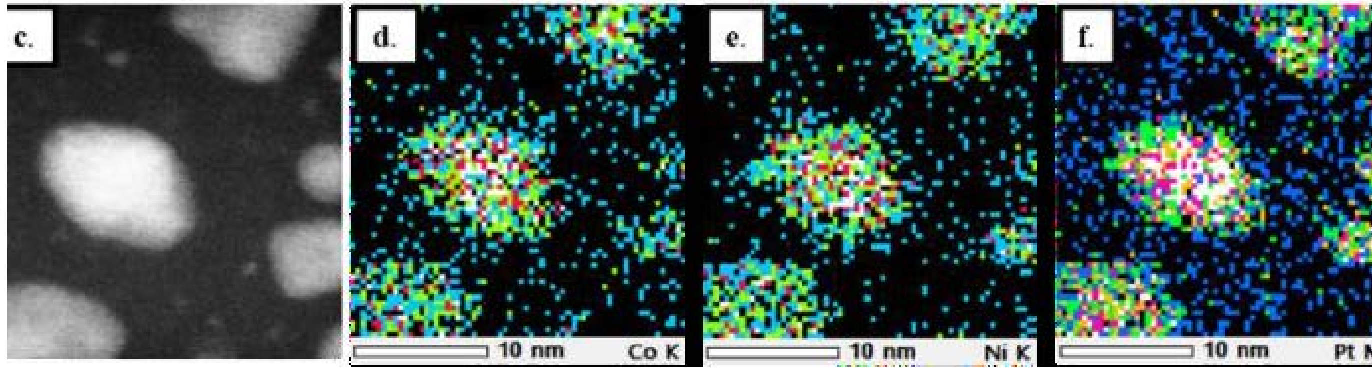
AuCoCuNiPt

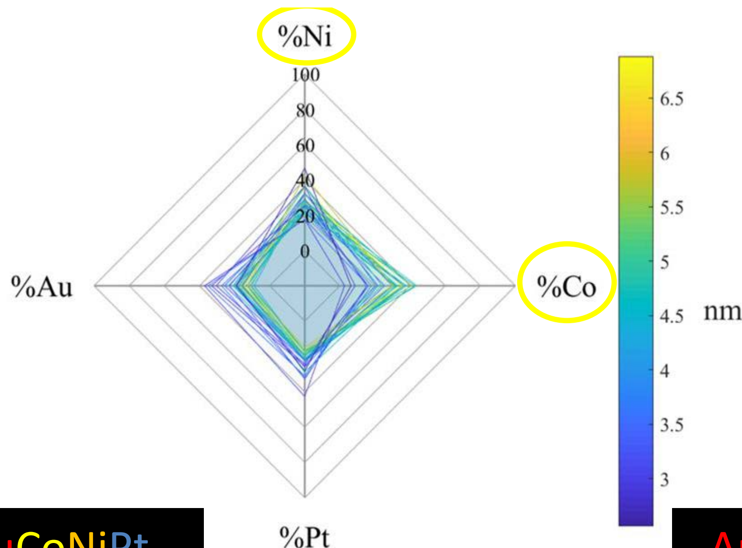
Structural properties of HEA NPs fabricated by PLD

CoNiPt

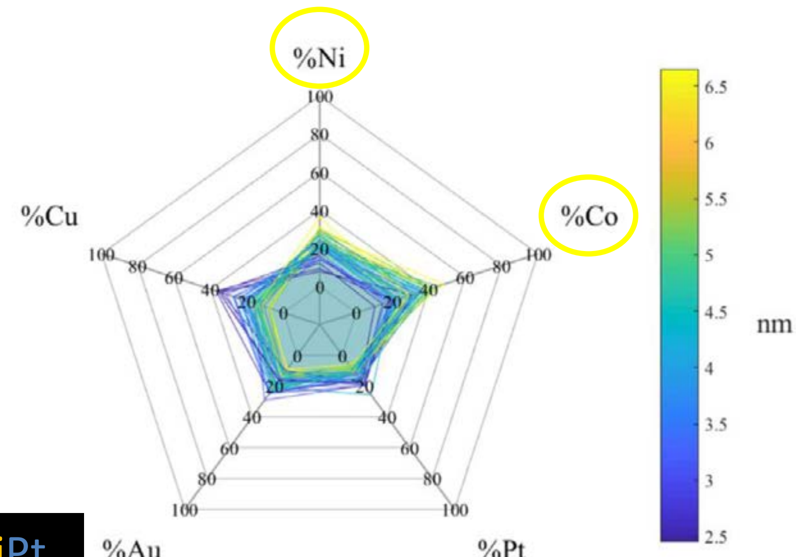
Chemical mapping and composition at the single NP level







AuCoNiPt



AuCoCuNiPt

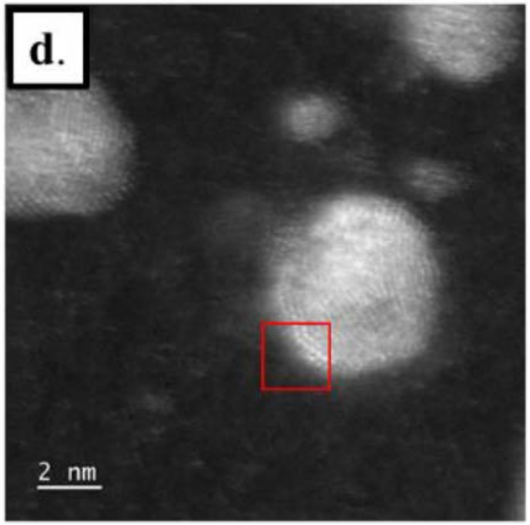
	All NPs	NPs with size < 5 nm	NPs with size > 5 nm	
at% of Co	28.16 ± 11.53	25.69	35.58	++
at% of Ni	29.01 ± 6.95	28.00	32.04	++
at% of Pt	23.10 ± 6.14	24.87	17.79	--
at% of Au	19.72 ± 7.42	21.43	14.59	--

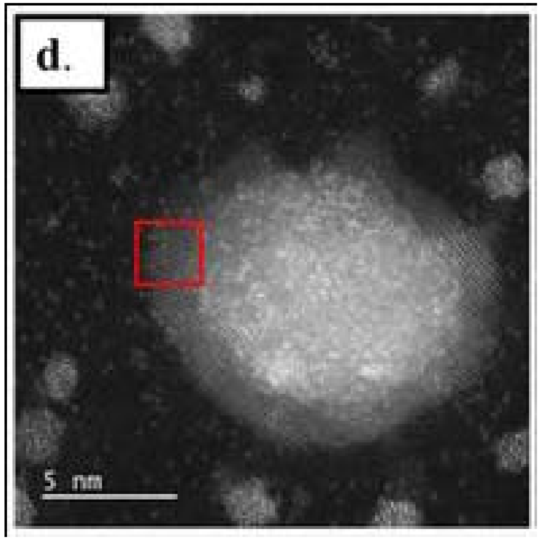
	All NPs	NPs with size < 4 nm	NPs with size > 4 nm	
at% of Co	29.61 ± 9.07	23.86	33.91	++
at% of Ni	21.90 ± 5.85	17.71	24.79	++
at% of Cu	18.38 ± 7.74	24.04	14.26	--
at% of Pt	13.05 ± 4.03	15.57	11.33	--
at% of Au	17.06 ± 4.85	18.82	15.72	--

Structural properties of HEA NPs fabricated by PLD

CoCuNiPt

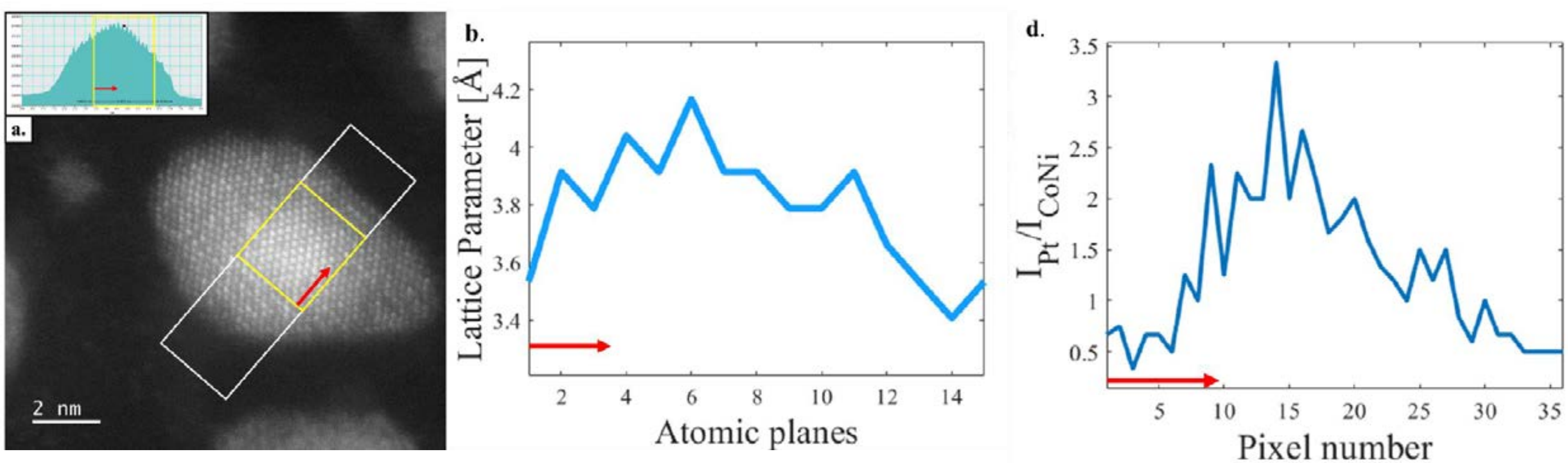
AuCoCuNiPt





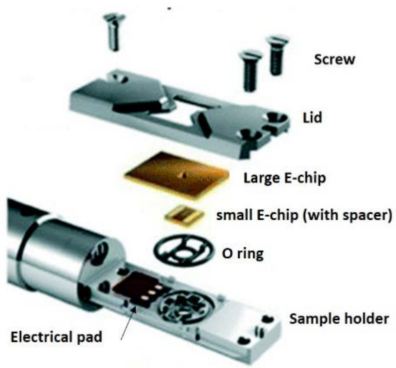
Deviating from the equiatomic composition induces phase separation

$Co_{28}Ni_{28}Pt_{45}$

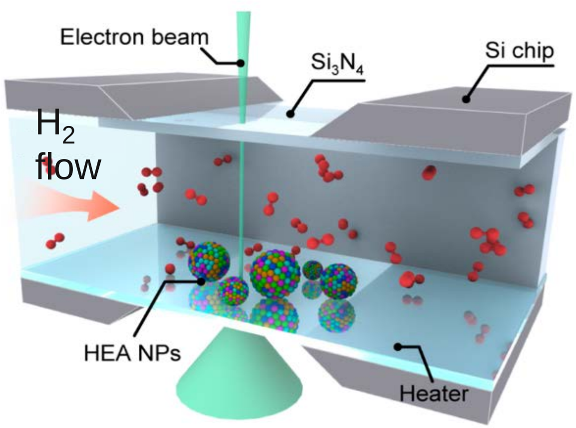


What's next ?

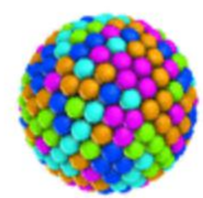
Evaluating the potential of HEA NPs for H storage and modeling



® Protochips



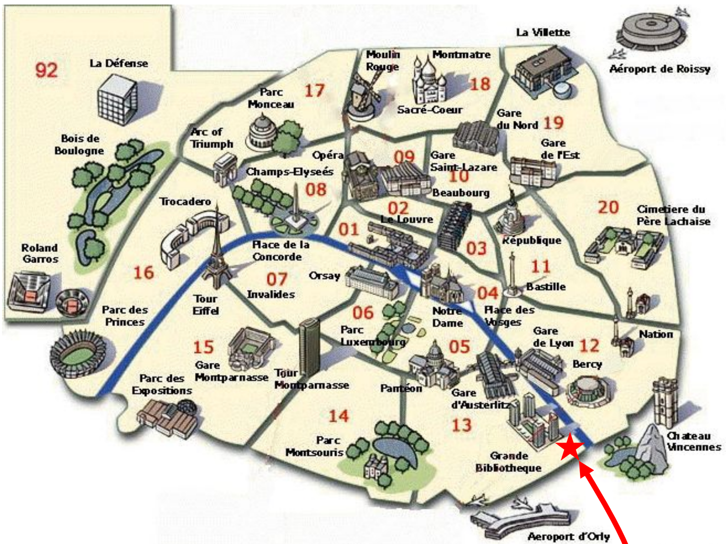
Atomic potentials for ternary CoPtNi alloys under development (LEM + CiNAM)



Collaboration with Claudia Zlotea (ICMPE) and TotalEnergies

Collaboration with Celine Varvenne (CiNAM)

National TEM user facility

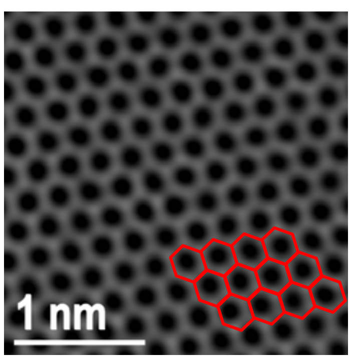


MPQ Lab @
University of Paris Cité

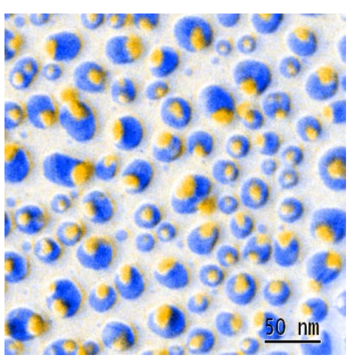
metsa

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

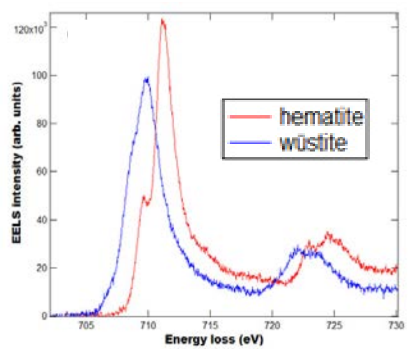
Sub-Angstrom imaging



Chemical mapping

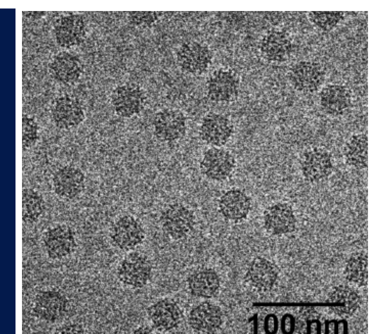


EELS spectroscopy



3D Imaging

Cryo TEM



Thank you

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

LABORATOIRE D'ETUDE DES MICROSTRUCTURES

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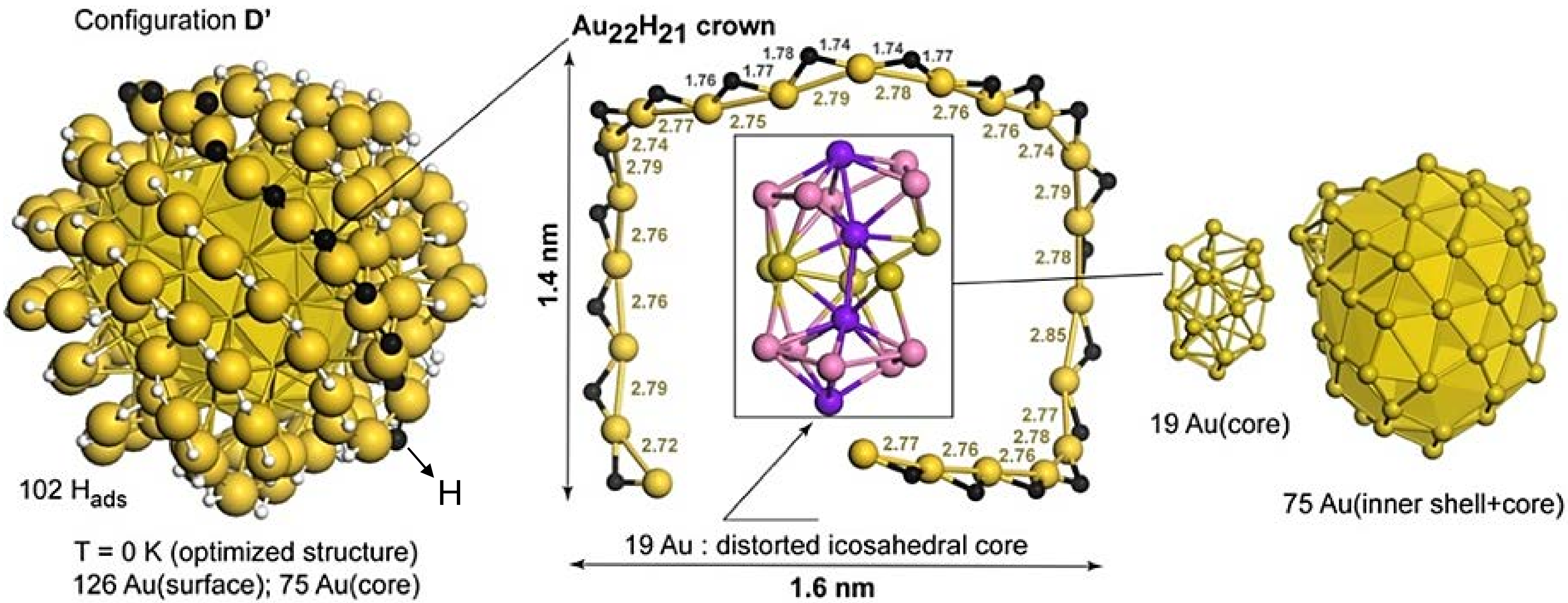
Kinanti Aliyah

Foundings :

cnrs
S-E-A-M
NanoSciences ILE-DE-FRANCE
îledeFrance
ANR PROJET FINANCÉ PAR L'ANR - PROJECT FUNDED BY THE ANR

Strong Au – H interaction



Strong Au-H interaction :

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

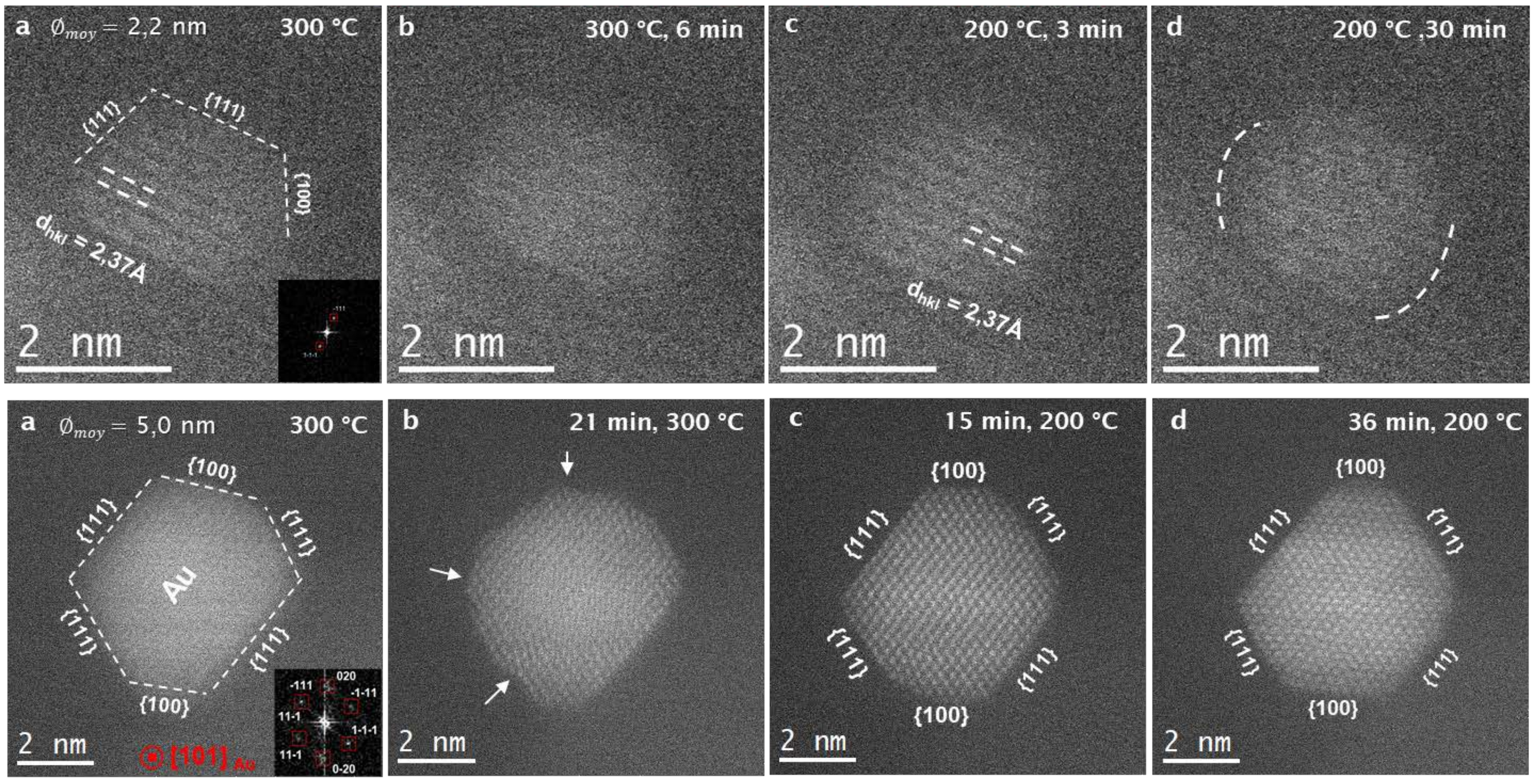
Nassereddine, Abdallah, Qing Wang, David Loffreda, Christian Ricolleau, Damien Alloyeau, Catherine Louis, Laurent Delannoy, Jaysen Nelayah, and Hazar Guesmi. Small (2021).

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

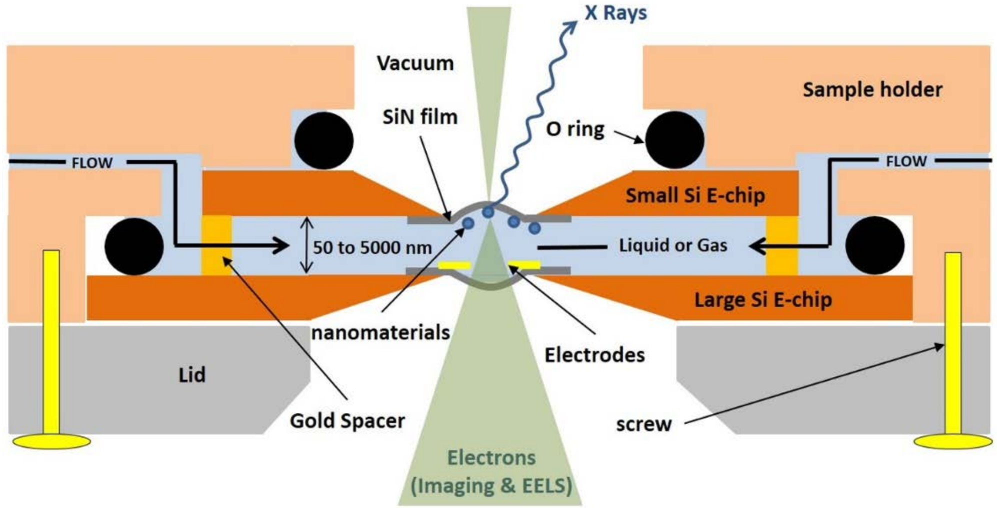


- Stable FCC structure
- Morphological change : interaction with C_4H_6

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



- Poseidon select
- Atmosphere
- Axon

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Materials Sciences — Nucleation and growth of nanomaterials

Live sciences — Structure and dynamics of biomaterials

Earth Sciences — Bio-mineralization processes in realistic media

Ross, Science 350, 1490 (2015)
De jonge and Ross Nature Mat. 6, 695 (2011)