Ecole Technologique des Plasmas Froids
17èmes journées du réseau
13-16 octobre 2024 - Carry-le-Rouet
Réseau Plasmas Froids

Nucleation and growth of nanoparticles in liquid phase

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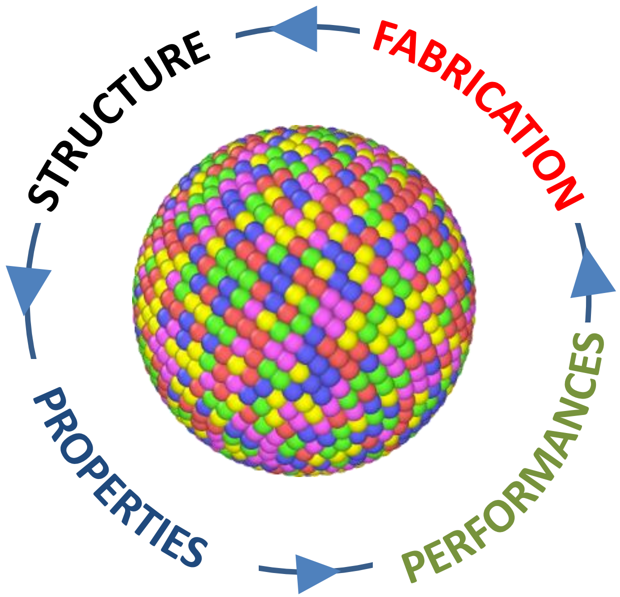
MPQ
Université Paris Cité

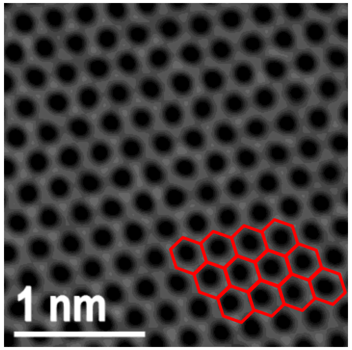
National EM user facility



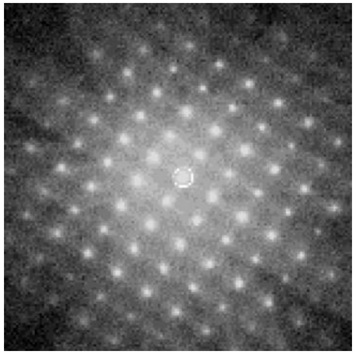
metsa

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

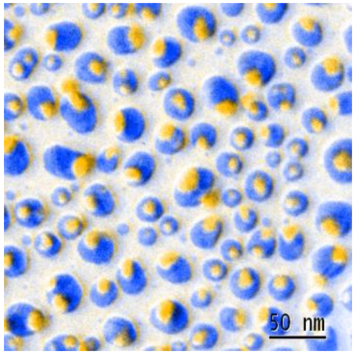
Sub-Angstrom imaging



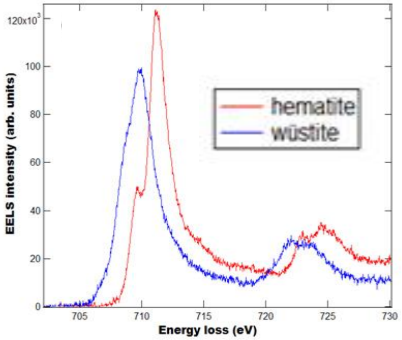
Electron diffraction



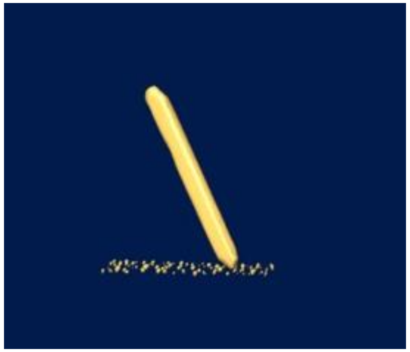
Chemical mapping



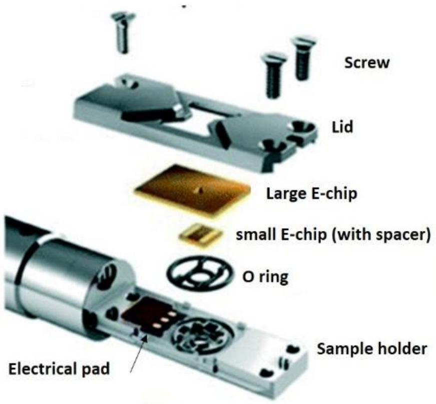
EELS spectroscopy

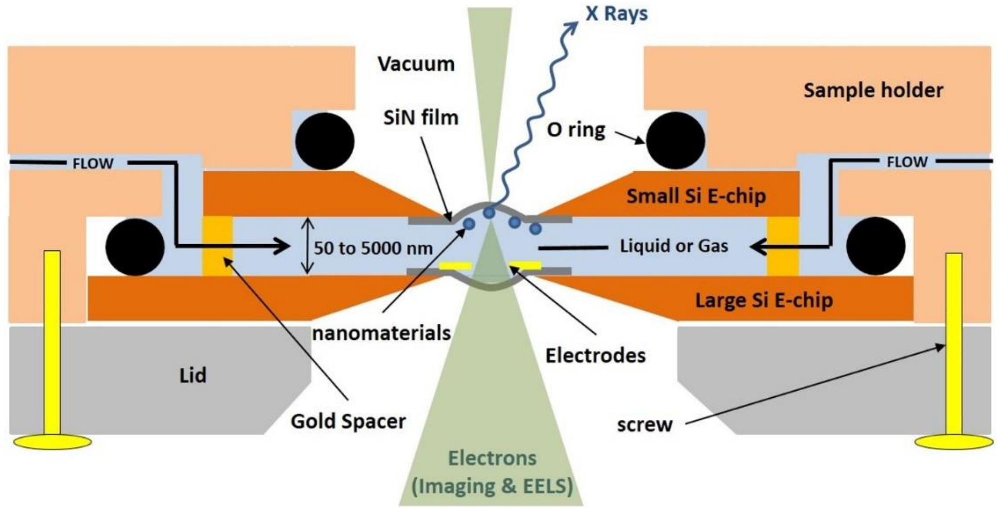


3D Imaging



Nanomaterials dynamics in their formation and application media

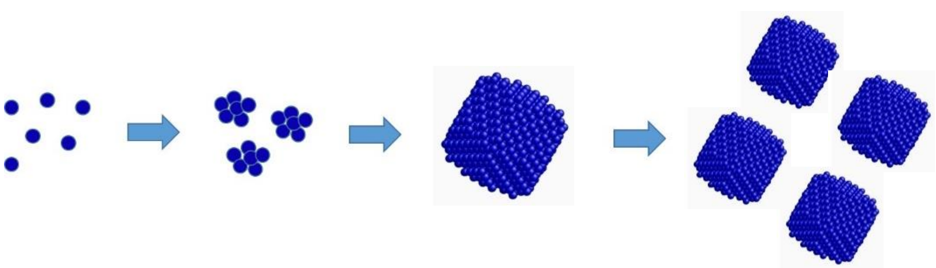




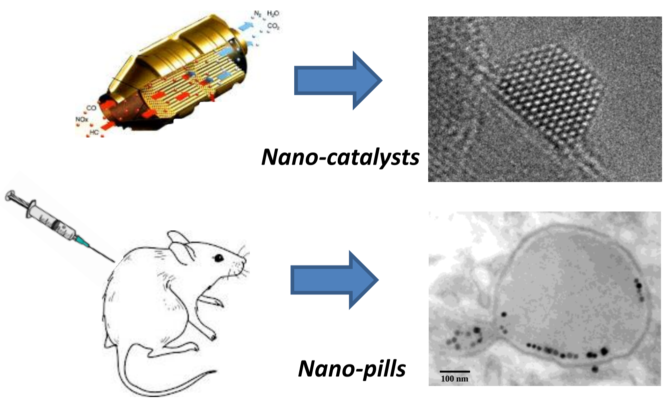
- Poseidon select
- Atmosphere

® Protochips

De jonge and Ross
Nature Mat. 6, 695 (2011)

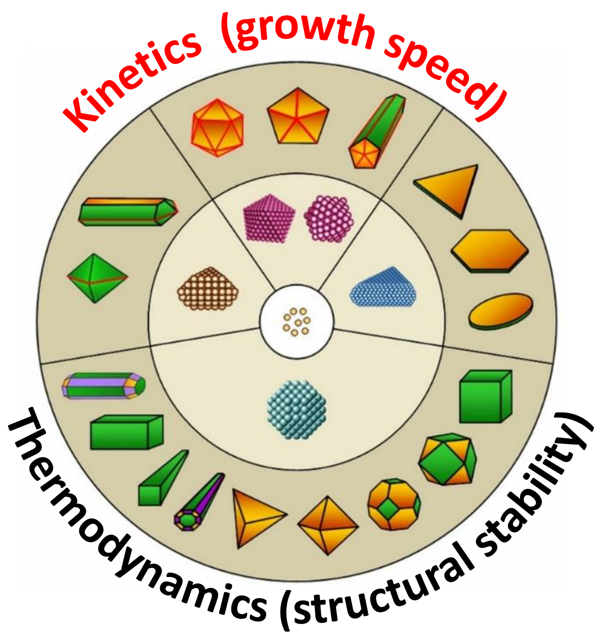


Nucleation, growth and self assemby

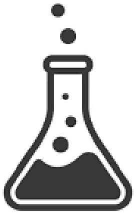


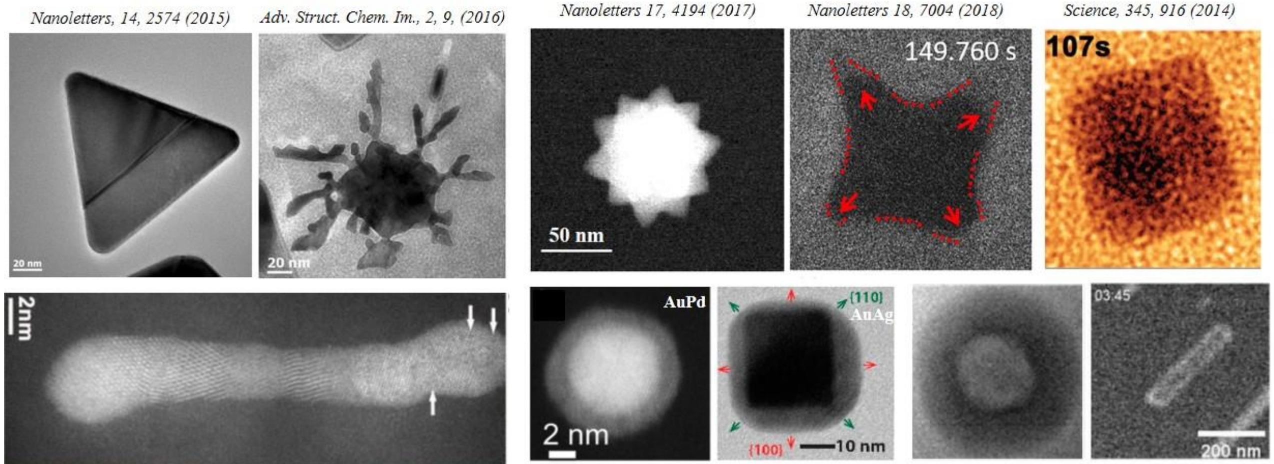
Transformation & degradation

Nucleation and growth of metal nanoparticles



- Seed-mediated synthesis
- Defect-driven growth
- Face blocking methods
- Kinetically-controlled formation
- Plasmon mediated growth
- …





Au nanoplates — *Nanoletters, 14, 2574 (2015)*
Au nanodendrites — *Adv. Struct. Chem. Im., 2, 9, (2016)*
Au and Pd Nanostars — *Nanoletters 17, 4194 (2017)*; *Nanoletters 18, 7004 (2018)*
Pt Nanocubes — *Science, 345, 916 (2014)*
$FePt_3$ Nanowires — *Science, 336, 1011 (2012)*
Core-shell nanostructures — *Nanolett. 13, 2964 (2013)*; *JACS. 138, 5190 (2016)*
Bi and Au hollow shells — *Nanolett. 13, 5715 (2013)*; *M&M. 24 244 (2018)*

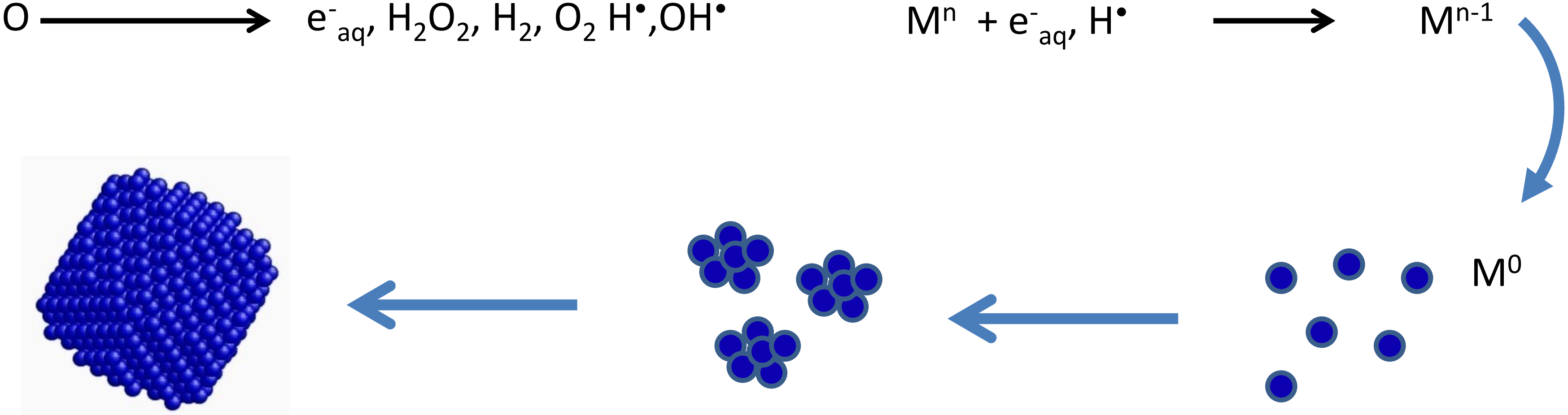
Radiolysis-driven nucleation and growth of gold nanoparticles

Radiolysis of water

$H_2O \xrightarrow{e^- \text{ beam}} e^-_{aq}, H_2O_2, H_2, O_2\ H^\bullet, OH^\bullet$

Reduction of metal precursor

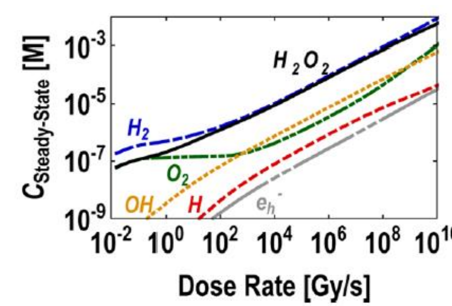
$M^n + e^-_{aq}, H^\bullet \longrightarrow M^{n-1}$



Growth

Nucleation

Electron dose is crucial !

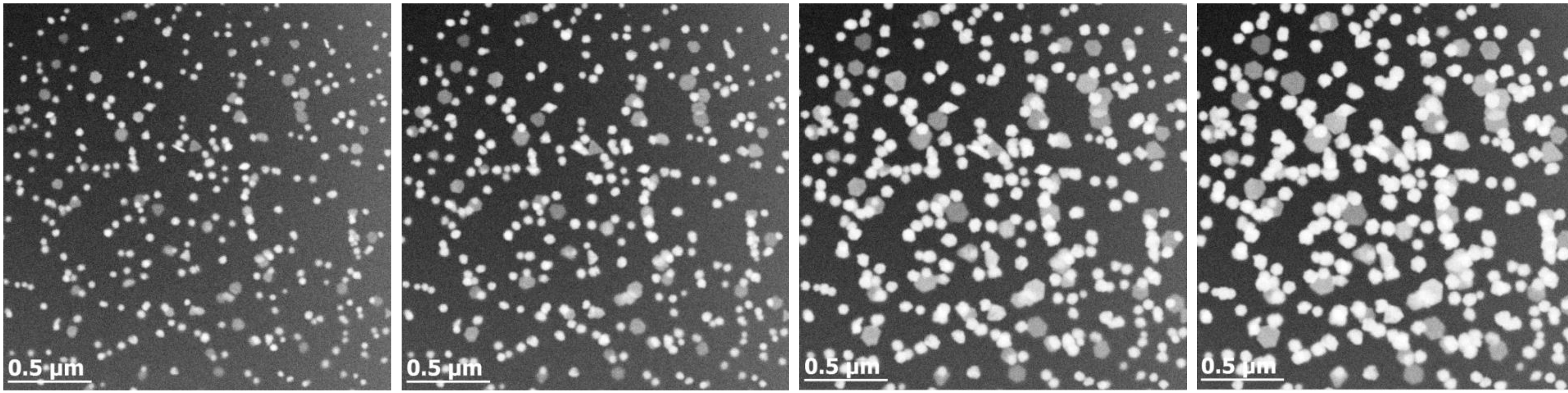


Distinguishing thermodynamic and kinetic effects

N. Schneider et al. Journal of physical chemistry C, 118, 22373

Controlling the kinetic of formation of nanostructures

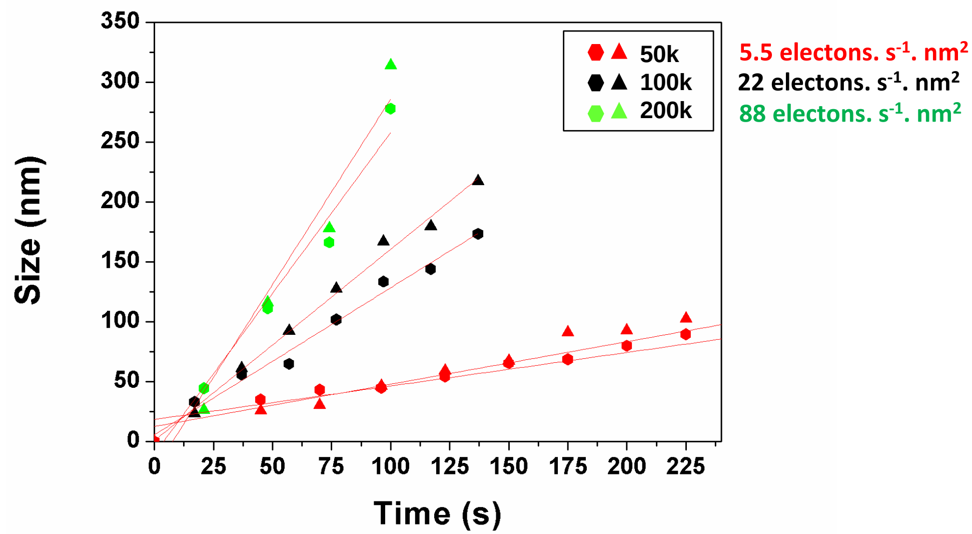
$HAuCl_4$ (1 mM) in water (dose rate of 22 electons. s^{-1}. nm^2)



15 sec | 60 sec | 105 sec | 150 sec

$$Dose\,(electrons/sA^2) = \frac{beam\ current\,(C/s)}{elementary\ charge\,(C/electron) * scanned\ area\,(A^2)}$$

1 electron . nm^2 . s^{-1} = 40 000 Gy . s^{-1} !!



Kinetics Vs Thermodynamic control

$V_{deposition} < V_{surface\ diffusion}$

Governed by thermodynamic

$V_{deposition} > V_{surface\ diffusion}$

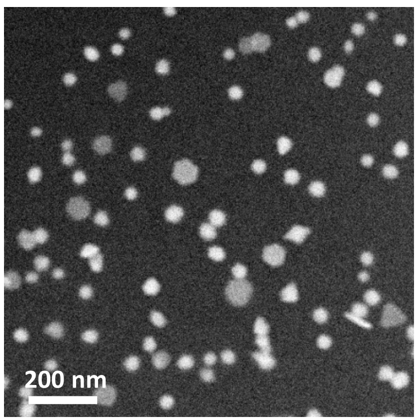
Governed by kinetics

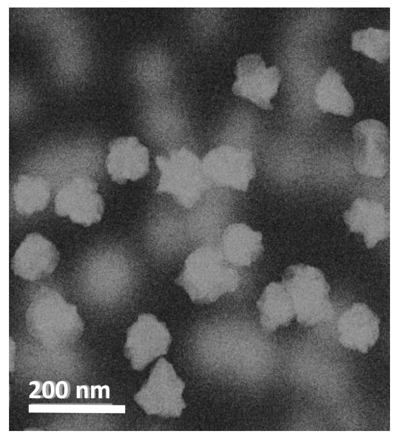
Electron dose →

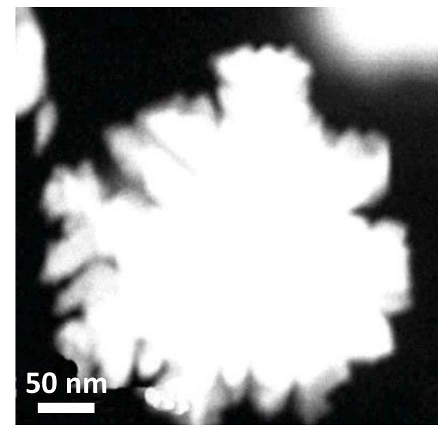
Magnification 100 k
dose = 10^6 Gy/s

Magnification 250 k
dose = 6.2 10^6 Gy/s

Magnification 400 k
dose = 1.6 10^7 Gy/s







The formation of facetted nanoparticles
requires reducing reaction rate < 3 atomic layers per seconds

Alloyeau et al. Nanoletters 15, 2574 (2015)

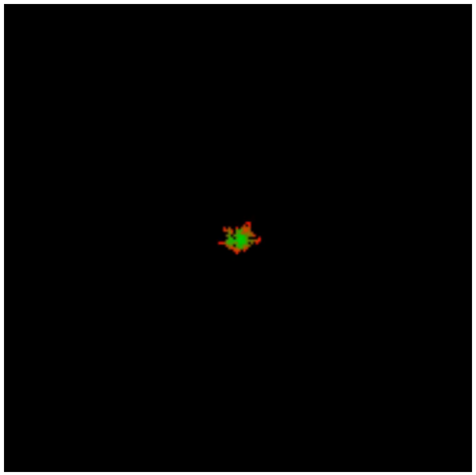
Diffusion - limited growth

Punta Nizuc (Cancun)

Diffusion - limited growth

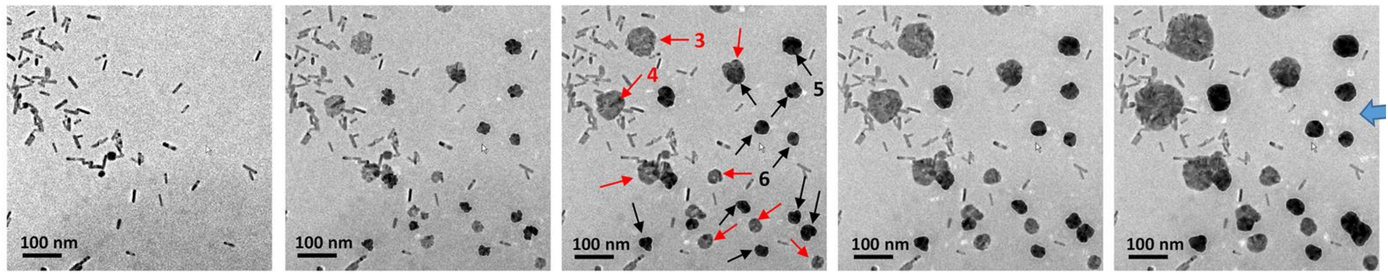
Eden model 1961
(growth in rich environment)

Collaboration with Y. le Bouar (LEM, ONERA)

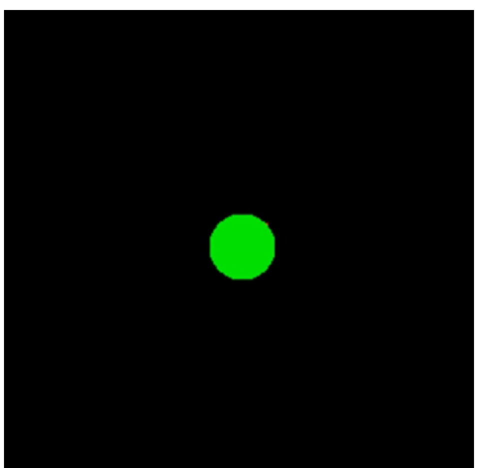


Pristine area

0 | 7 s | 14 s | 21 s | 35 s

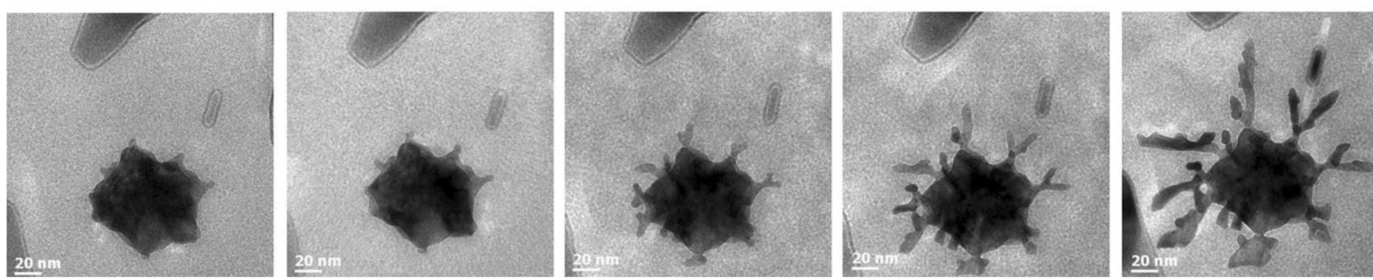


Diffusion limited aggregation (DLA)
« food is far away »



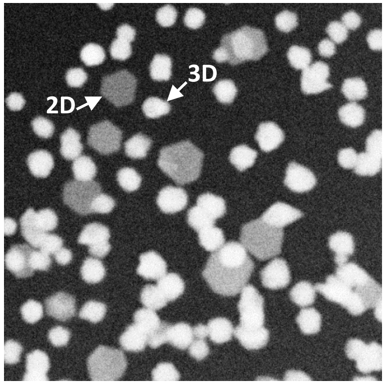
Pre-exposed area

0 | 10 s | 20 s | 30 s | 45 s



***Ahmad et al. Advanced Structural and Chemical Imaging* 2, 9 (2016)**

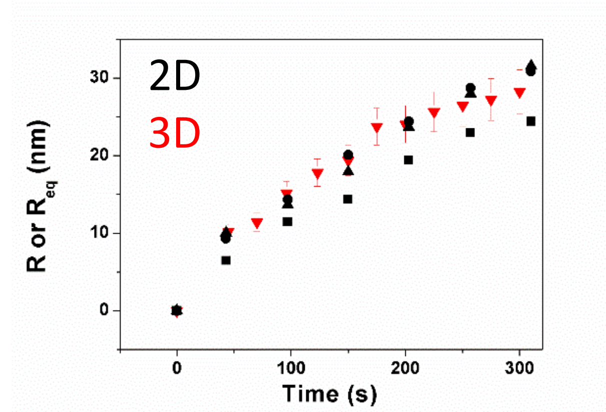
What about the shape of faceted nanoparticles ??

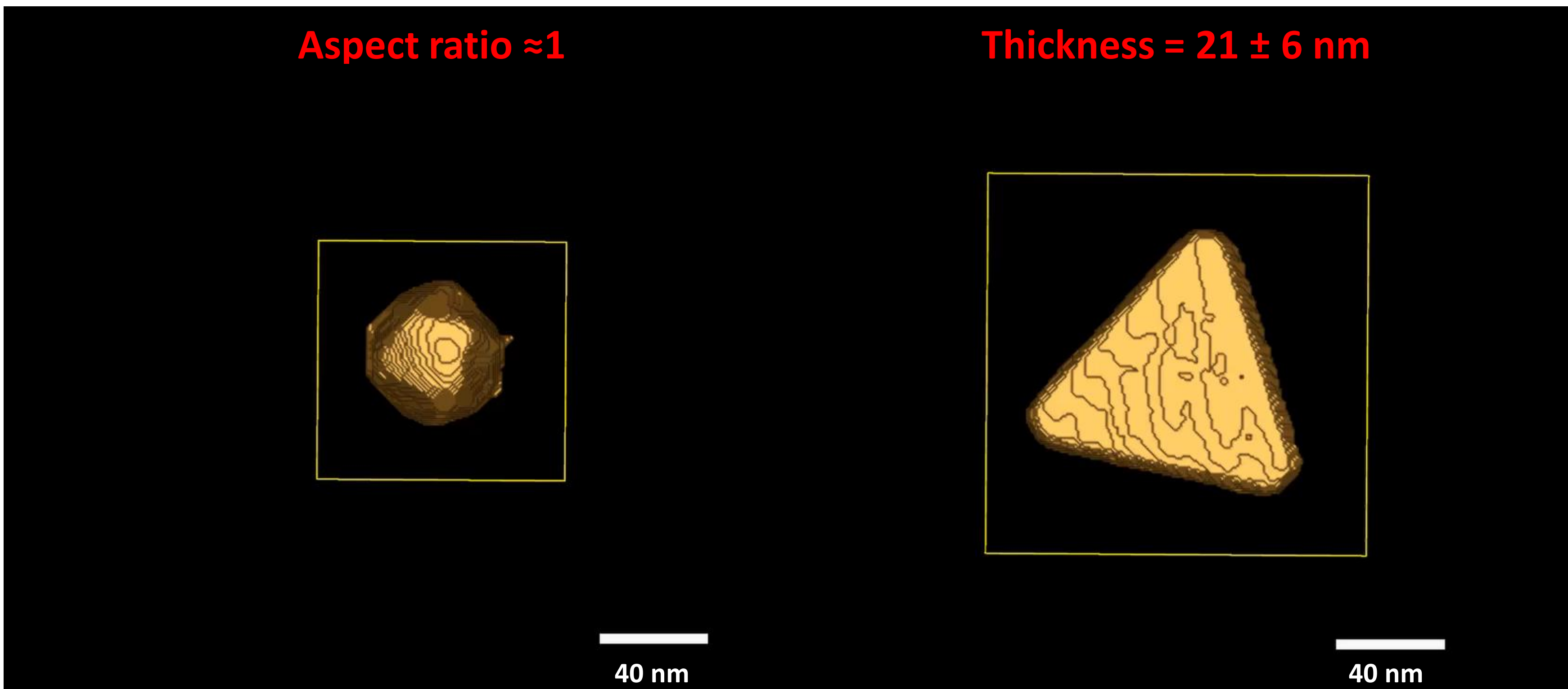


Electron tomography (± 60°)

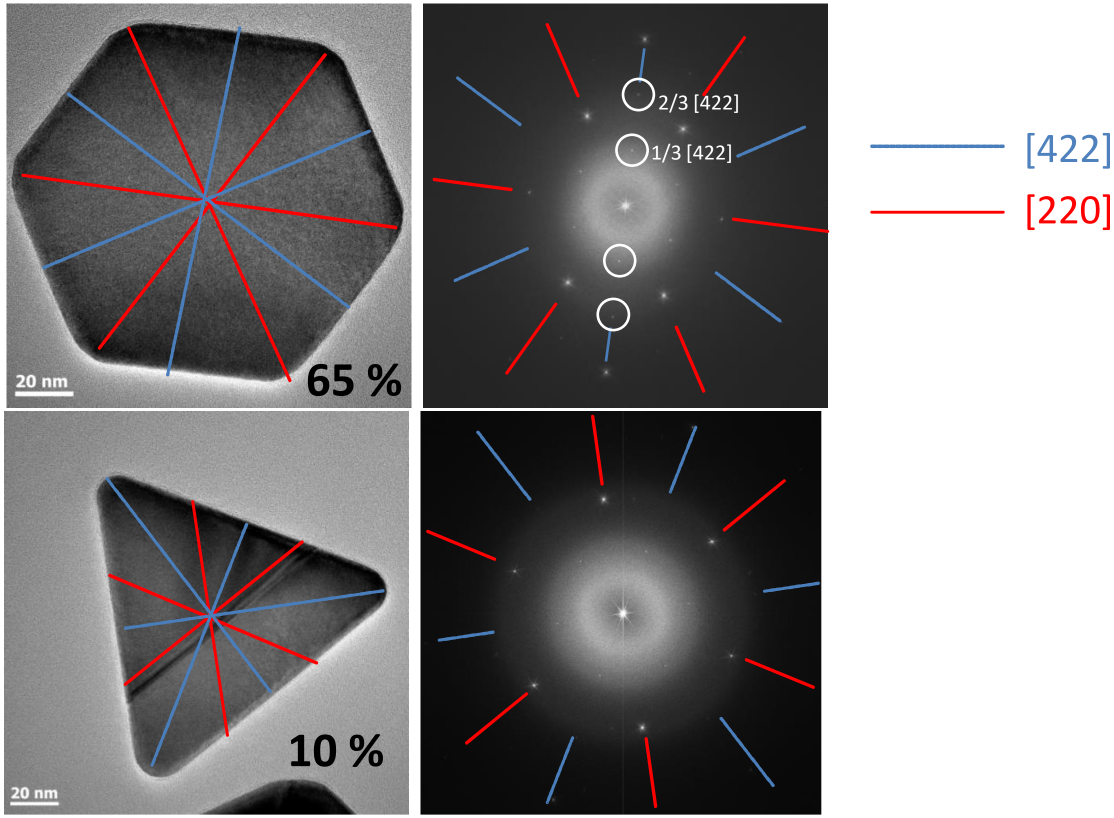
+ DART reconstruction

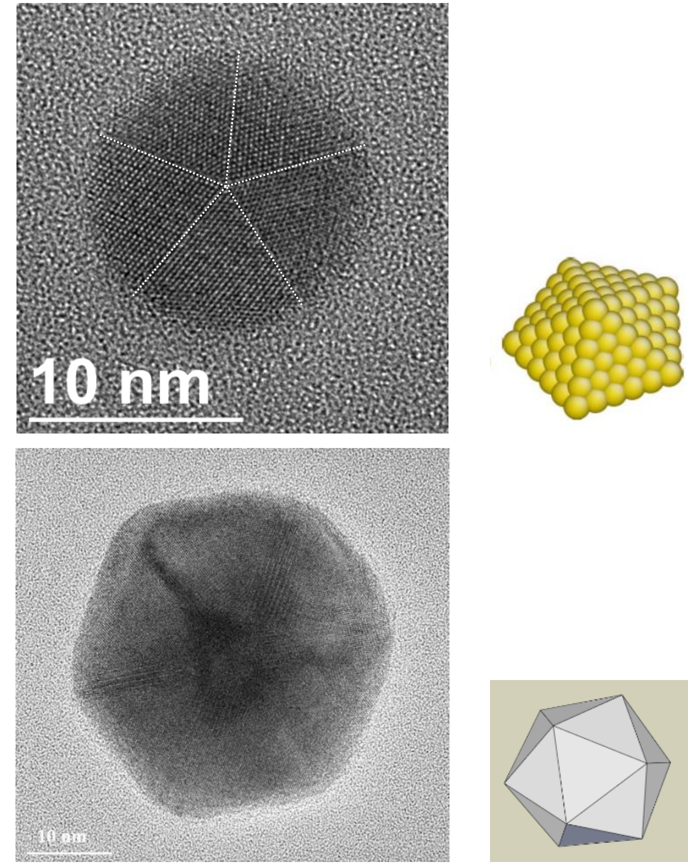
(collaboration with Ovidiu Ersen, IPCMS, Strasbourg)

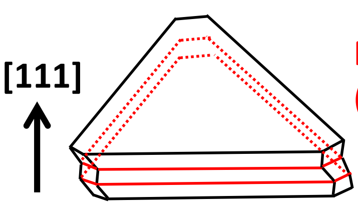




Defect - driven growth

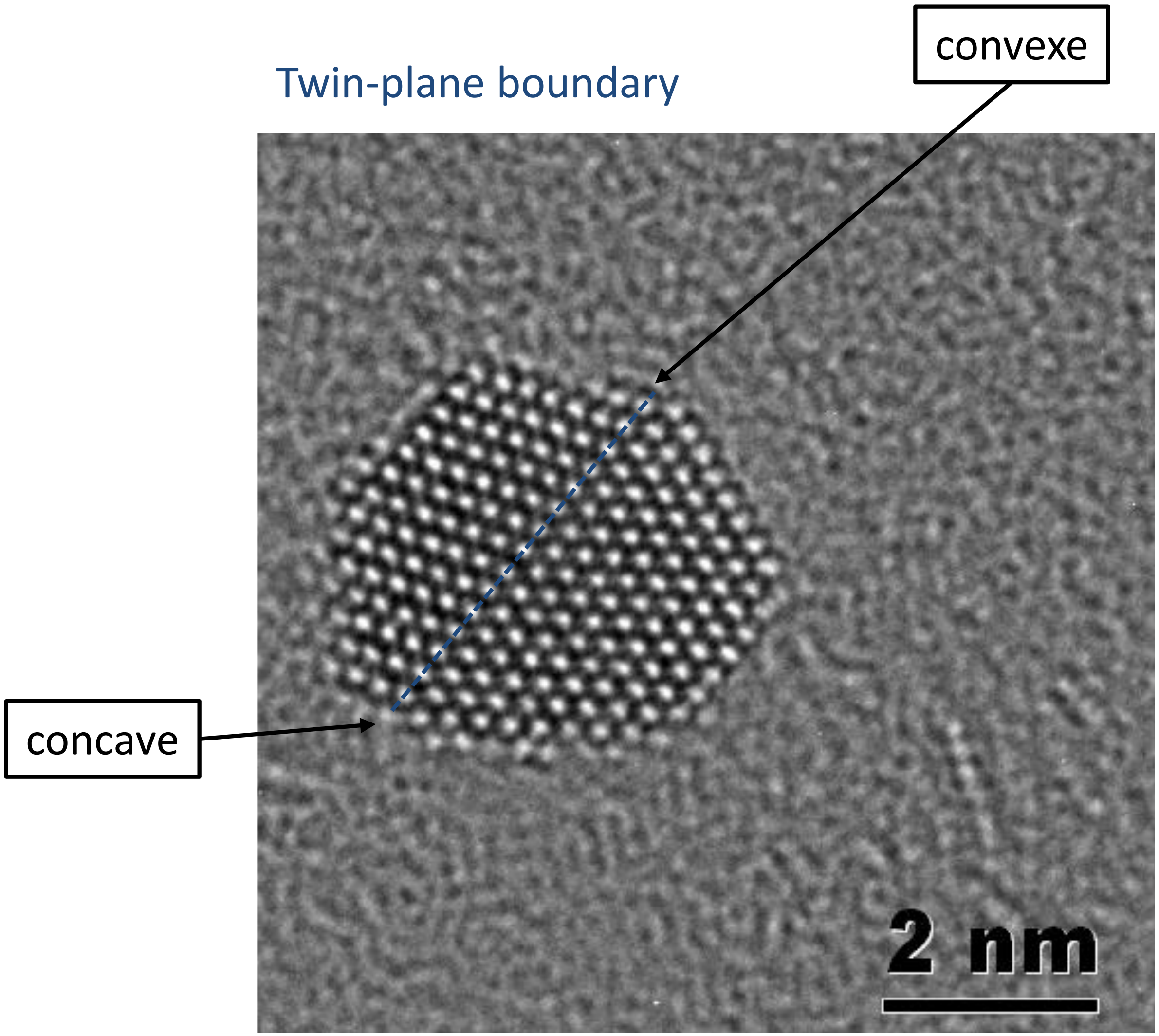




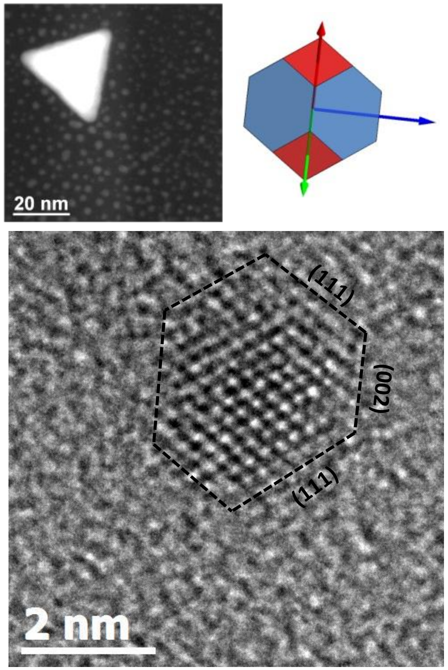


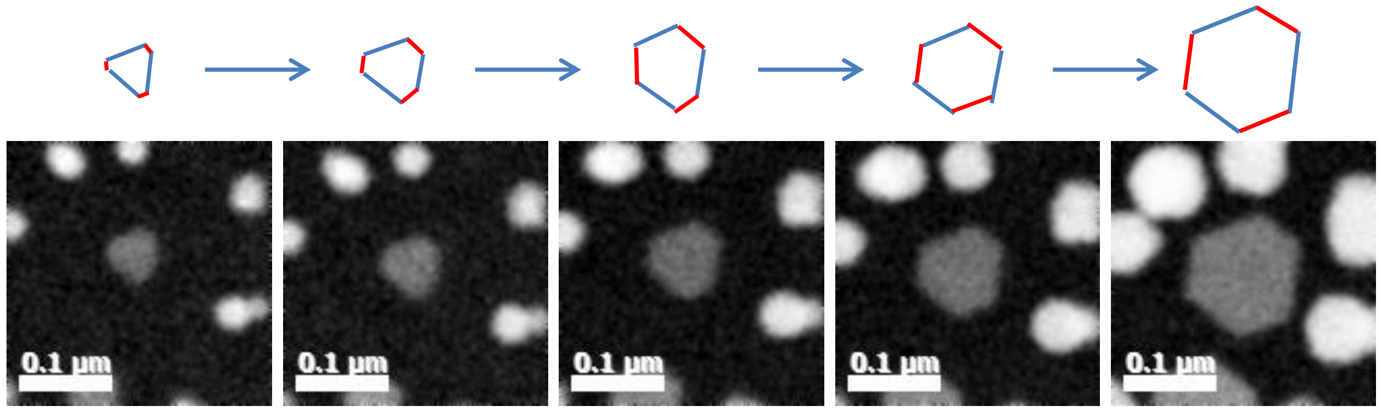
Planar defects
(Twin planes or stacking faults)

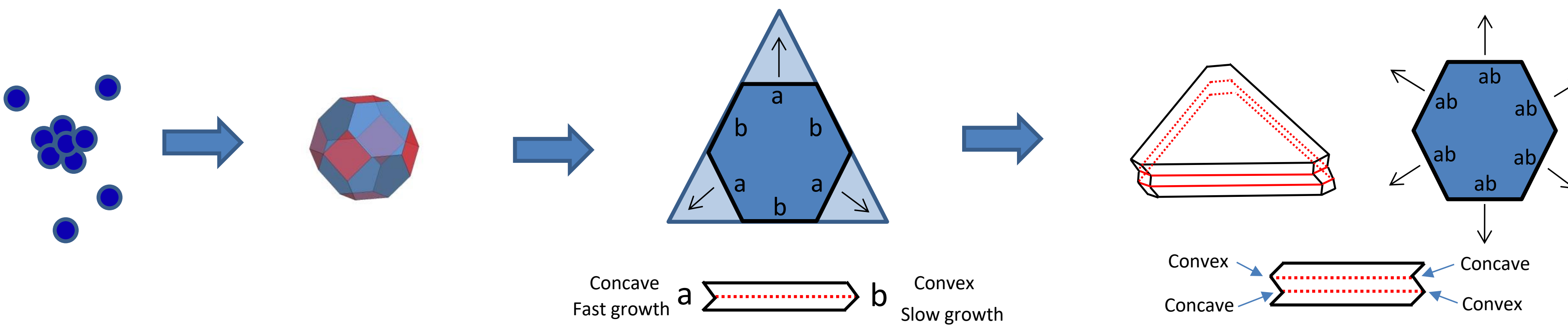
Defect - driven growth



Defect - driven growth



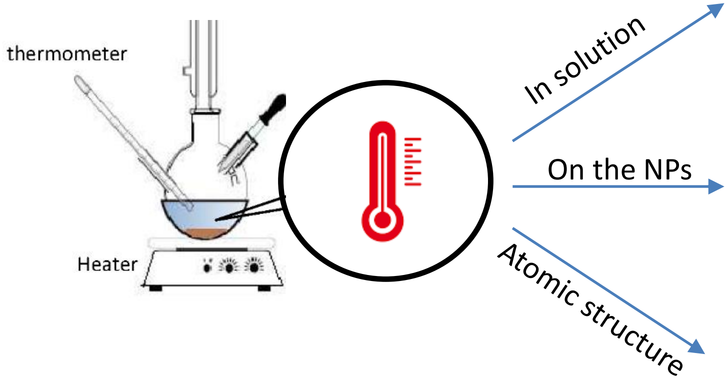




$$\Delta\mu = \gamma\Omega\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

Lonfton and Sigmund Adv. Fonct. Mater. 15, 1197 (2005)

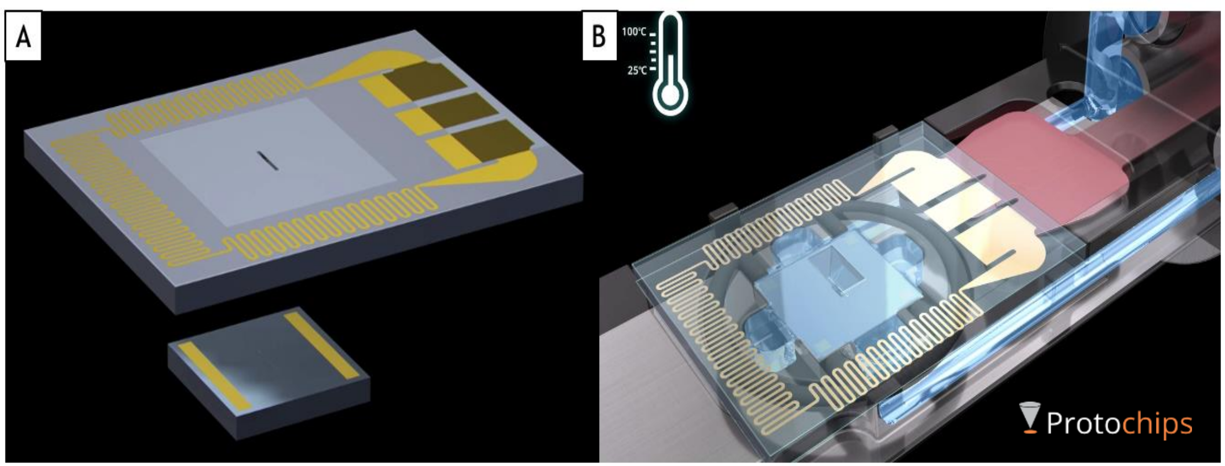
Temperature effects on gold nanoparticle formation



reaction, solubility and diffusion of metal precursors

nucleation, adsorption, desorption and diffusion of metal atoms, Ostwald ripening and coalescence

Thermodynamic equilibrium



Khelfa et al. JOVE methods 2021 (video article)

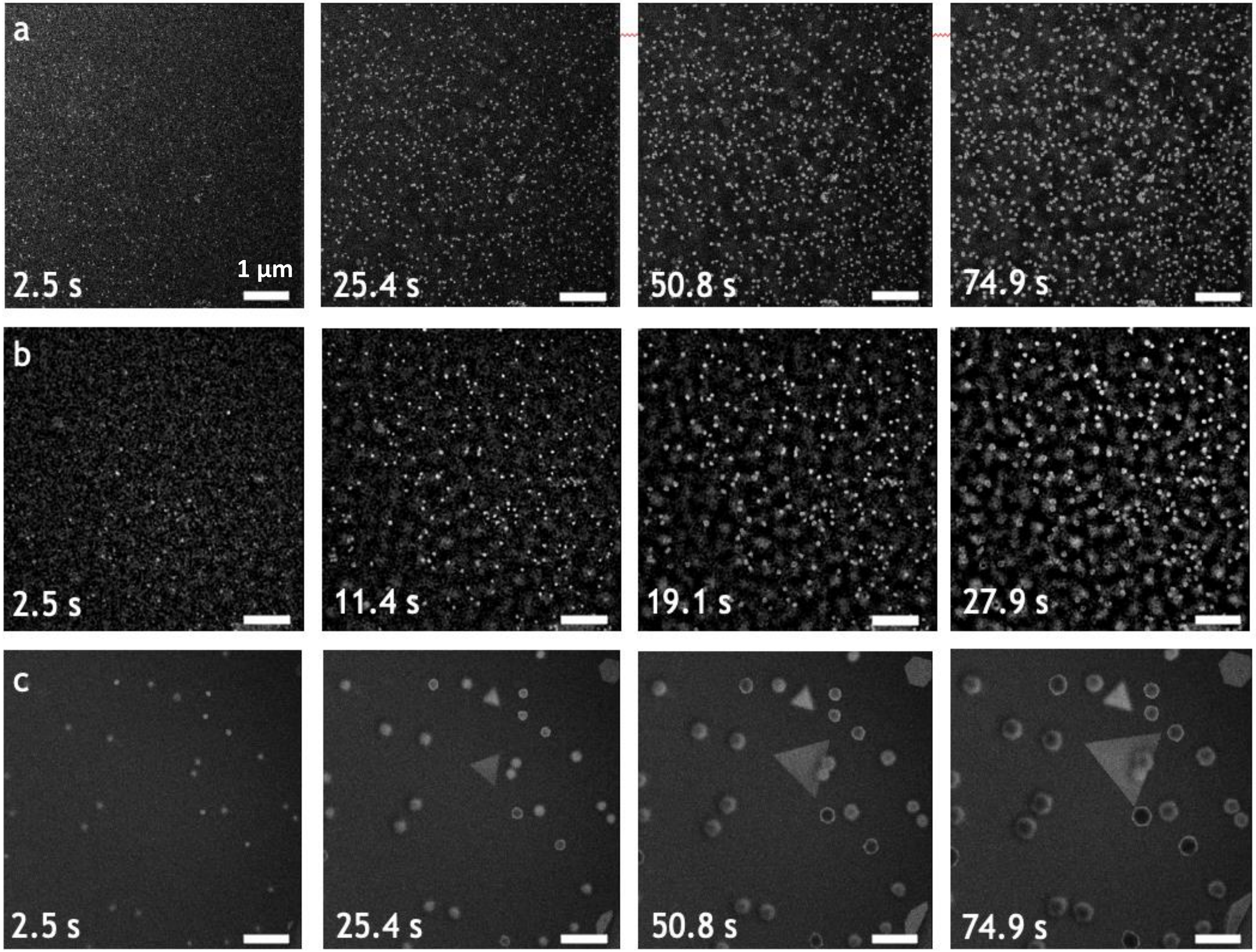
Temperature effects on gold nanoparticle formation

Very low dose rate experiments (3.4 electrons.nm^{-2}.s^{-1}) in 1 mM HAuCl4

25°C

50°C

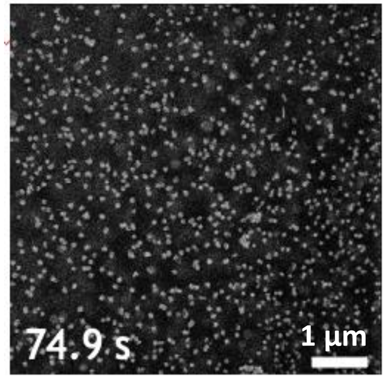
85°C



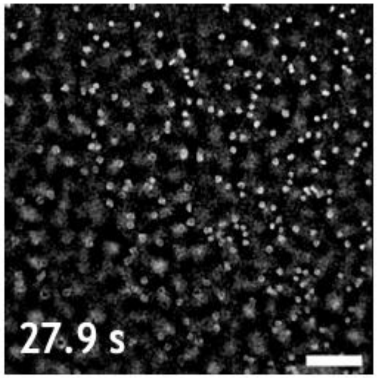
Khelfa et al. Advanced Materials 33, 2102514 (2021)

Temperature effects on the nucleation dynamics

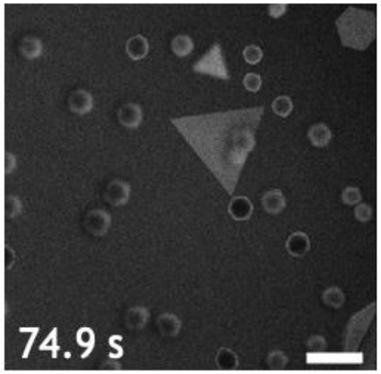
25°C

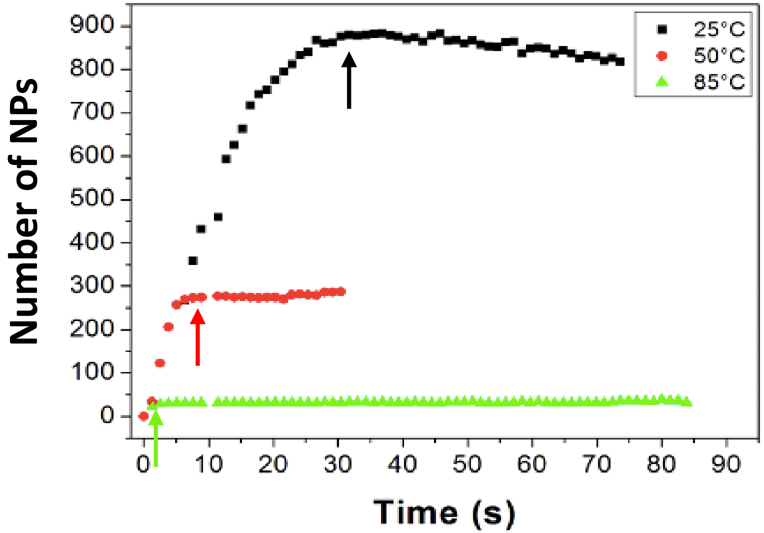


50°C

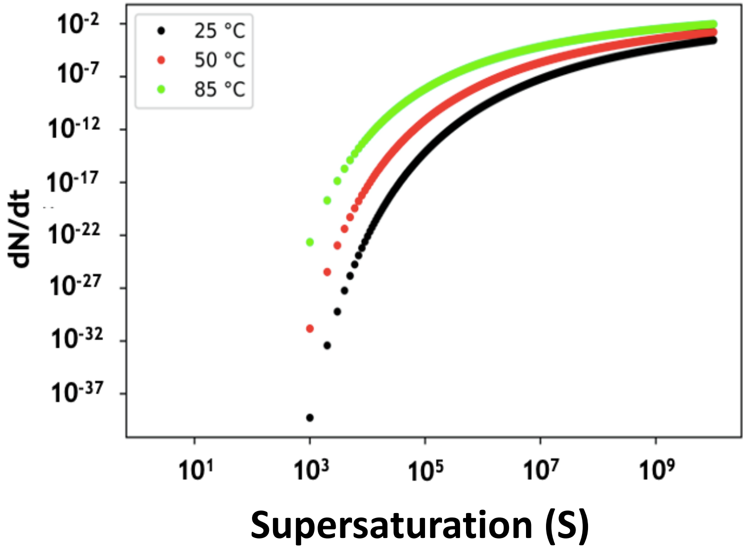


85°C





Nanoparticle density decreases with temperature because the nucleation period shortens



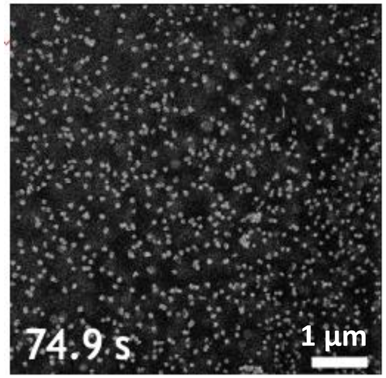
Nucleation theory

$$\frac{dN}{dt} = A\exp\left(-\frac{16\,\emptyset\pi\gamma^3 V_m^2}{3k_b^3 T^3 N_a (\ln S)^2}\right)$$

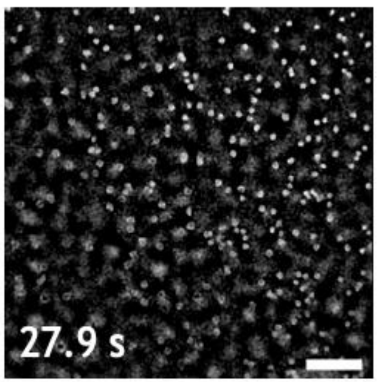
LaMer et al, *JACS* (1950)

Temperature effects on the nucleation dynamics

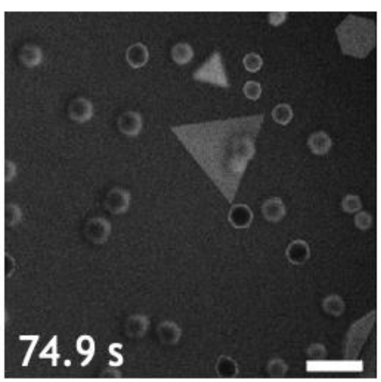
25°C

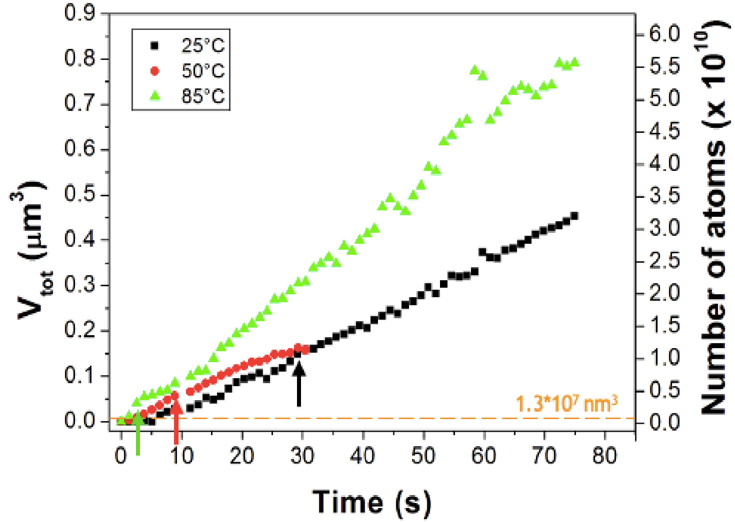


50°C



85°C





$$S = \frac{C_{Au}}{C_\infty}$$

C_{Au} decreases faster at high temperature but…

Saturated NaCl solution

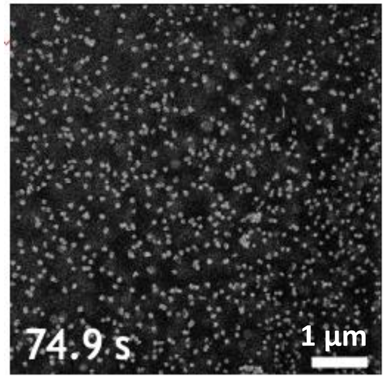
cold

hot

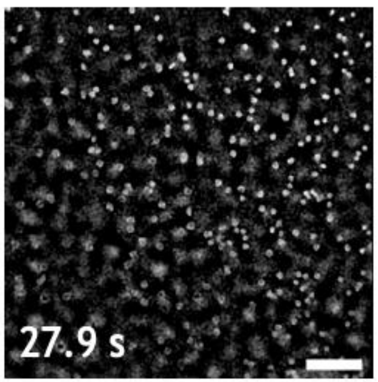
C_∞ increases with temperature

Temperature effects on the growth dynamics

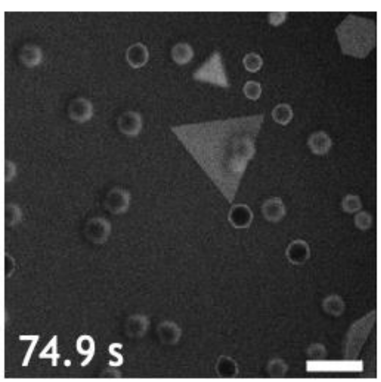
25°C

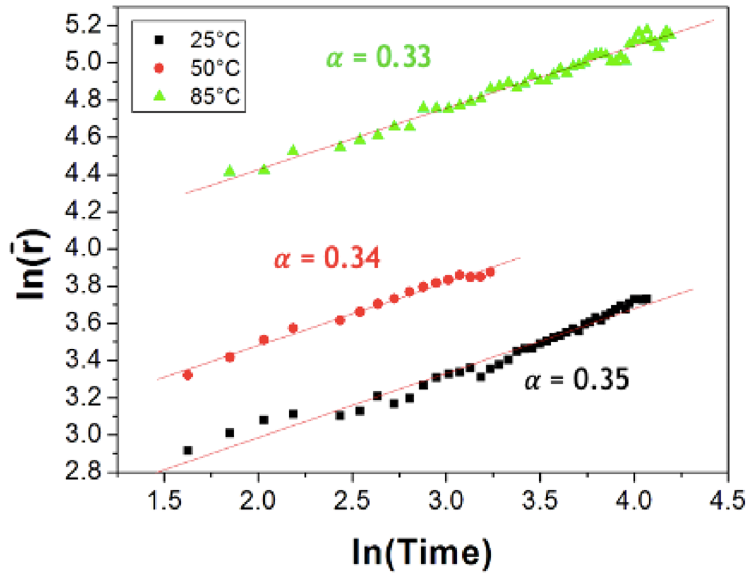


50°C



85°C

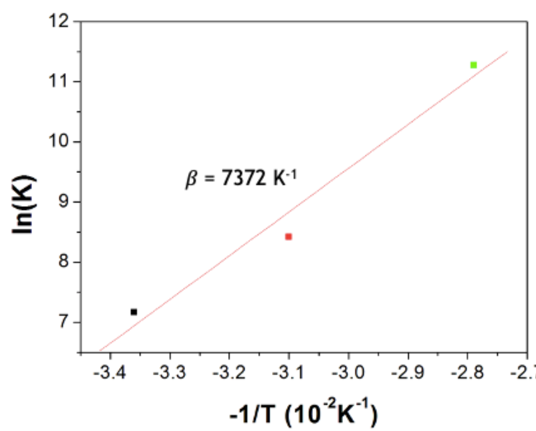




LSW theory (Diffusion-limited growth)

$$\bar{r}^3 = Kt$$

$$K = \frac{4\gamma V_m^2 C_\infty}{27\pi N_a \eta a}$$



$$C_\infty^{50°C} = 2.2 \times C_\infty^{25°C}$$

$$C_\infty^{85°C} = 22.6 \times C_\infty^{25°C}$$

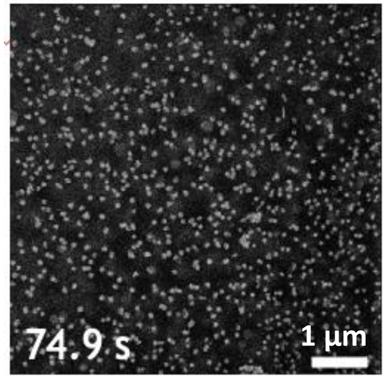
Activation energy for NP growth = 61 kJ.mol^{-1} (0.63 eV/atom)

SAXS and XANES Abecassis et al Langmuir 2010, 26, 13847

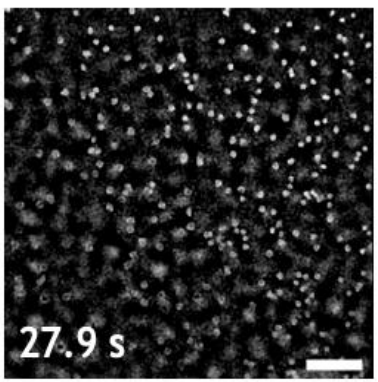
Solubility rules the nucleation dynamics

$$S = \frac{C_{Au}}{C_{\infty}}$$

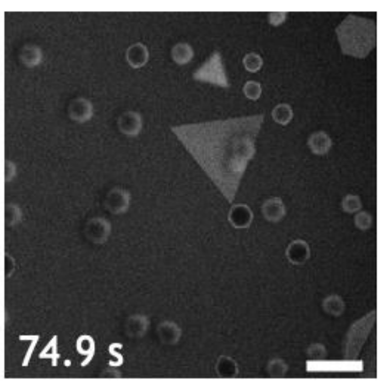
25°C

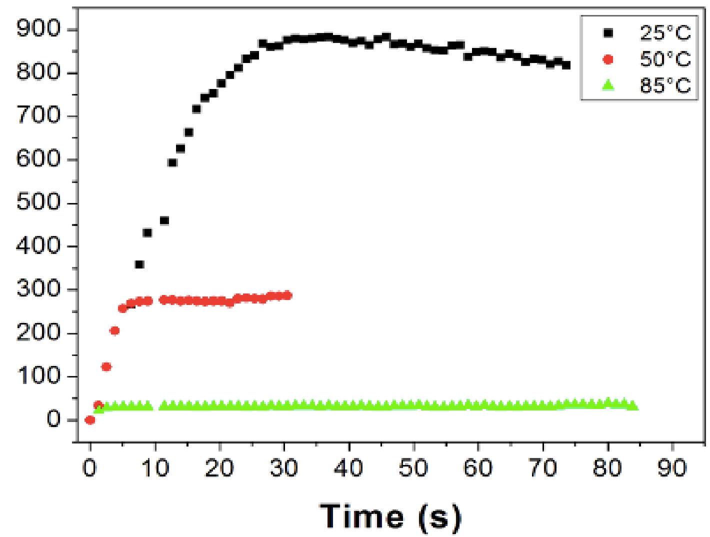


50°C



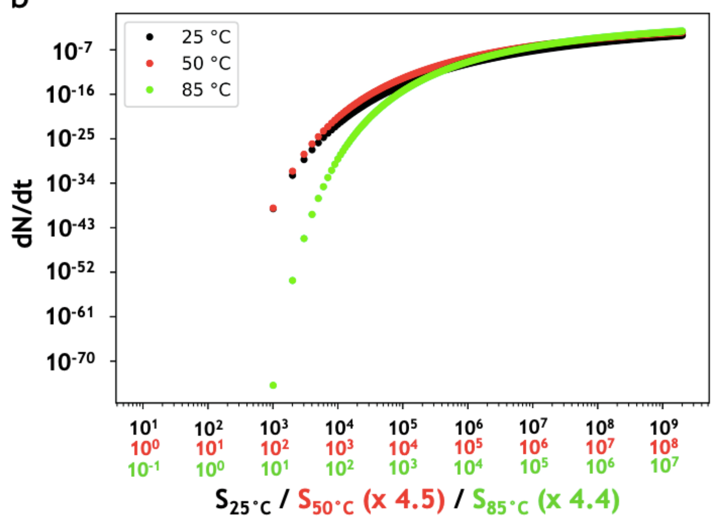
85°C





Experiments :
The nucleation period is reduced with temperature

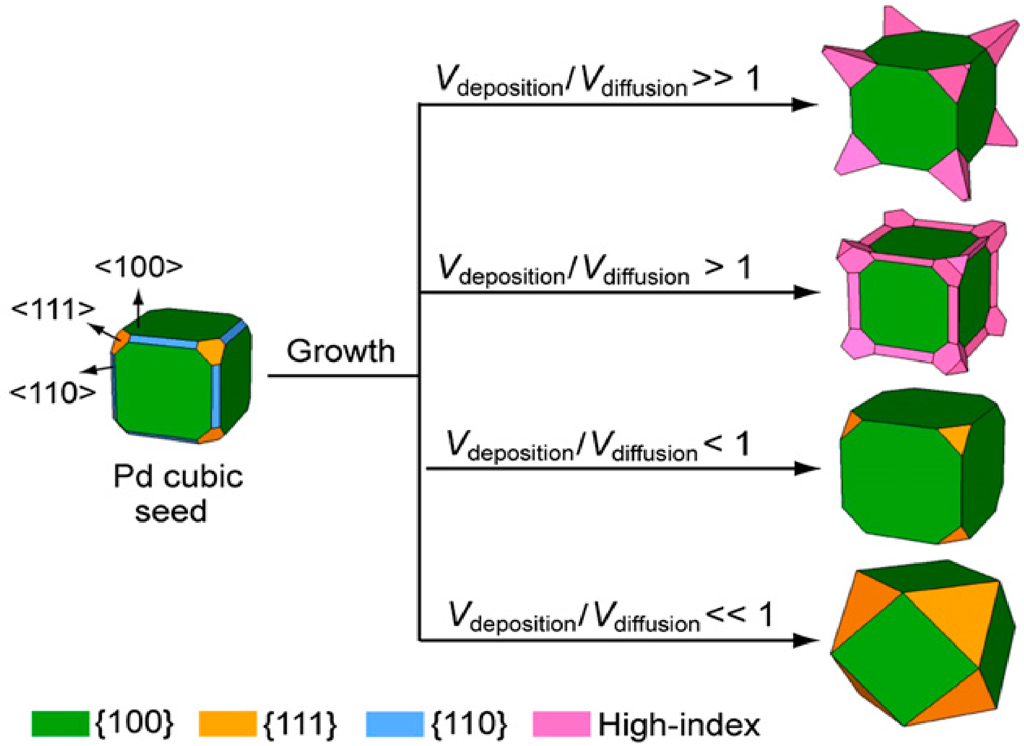
b



Nucleation theory with $C_{\infty}(T)$

$V_{deposition}$ / $V_{diffusion}$ ratio rules the shape of nanostructures

X. Xia et al. *Proceedings of the National Academy of Sciences* 2013, 110, 6669



In our the liquid cell TEM experiments

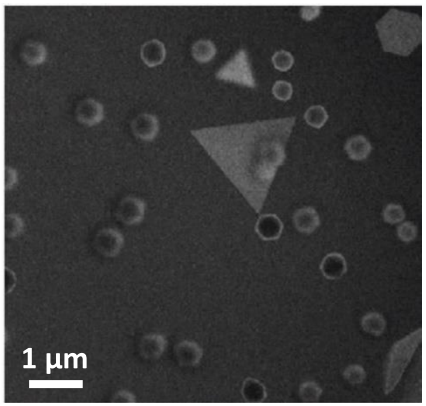
$V_{deposition}$ increases with dose rate and temperature
$V_{diffusion}$ increases only with temperature

$V_{deposition}$ / $V_{diffusion}$ ratio rules the shape of nanostructures

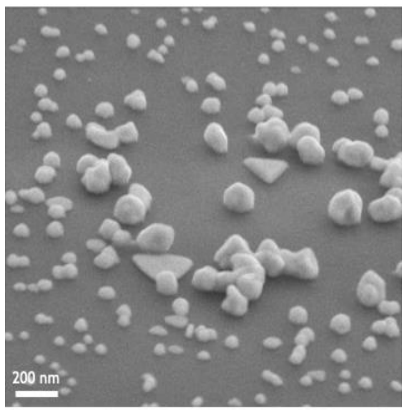
Low dose rate

High dose rate

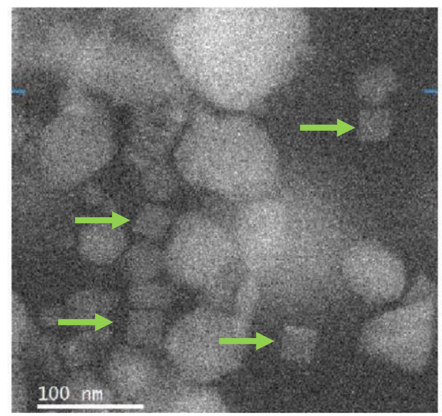
85°C



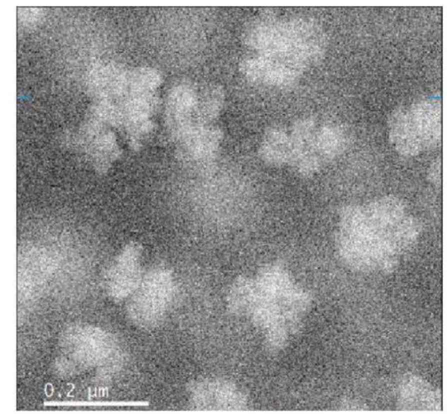
25°C



85°C



25°C



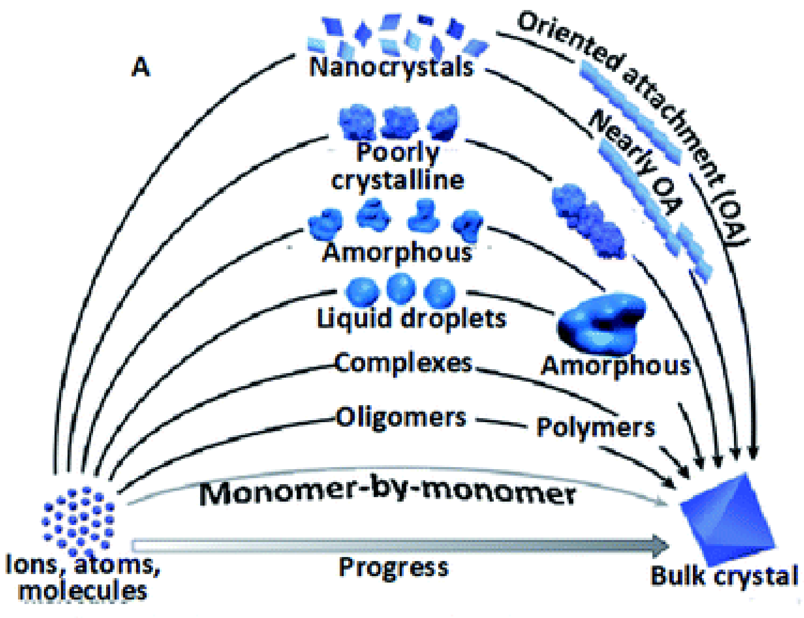
$V_{deposition}$ <<< $V_{diffusion}$ → **Faceted NPs With (111) surfaces**

$V_{deposition}$ < $V_{diffusion}$ → **Faceted NPs with (100) surfaces**

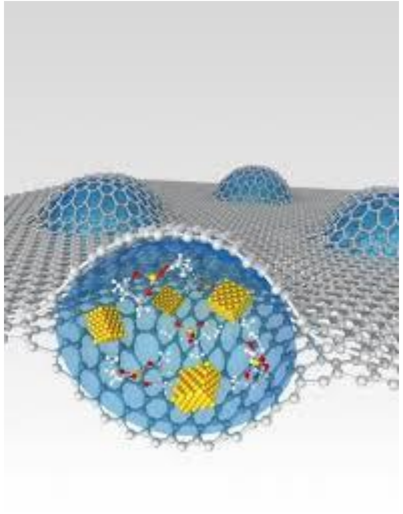
$V_{deposition}$ > $V_{diffusion}$ → **Dendritic NPs with rough surfaces (high index facets)**

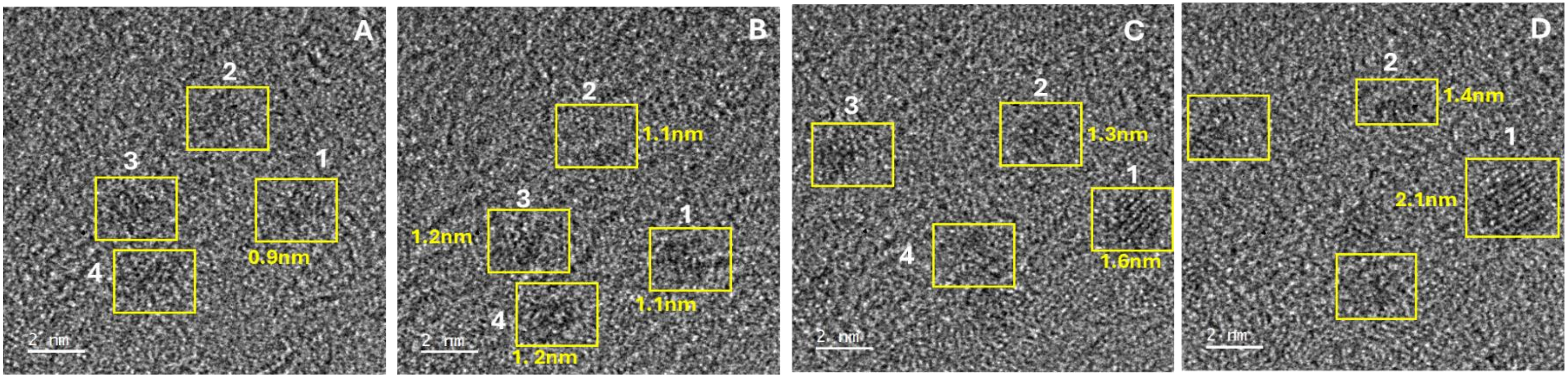
Khelfa et al. Advanced Materials 33, 2102514 (2021)

Nucleation : a non classical mechanisms



De Yoreo *Science*, 2015, 349, aaa6760



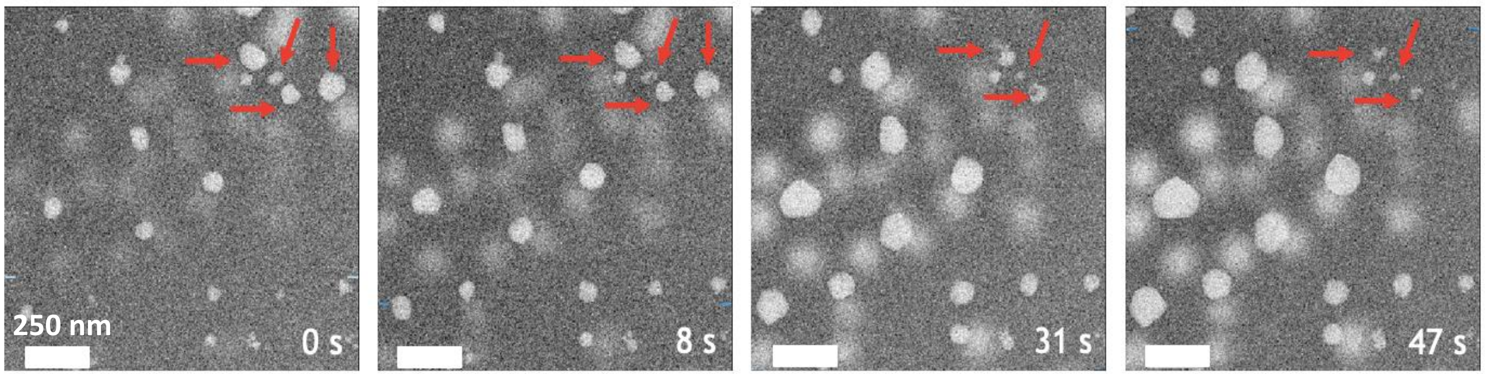


Amorphous crystline phase transition at 1.6 nm in gold NPs

Growth mecansisms : Oswald ripening

Idealistic view of Ostwald ripening:
the growth of larger NPs at the expense of the small ones.

85°C



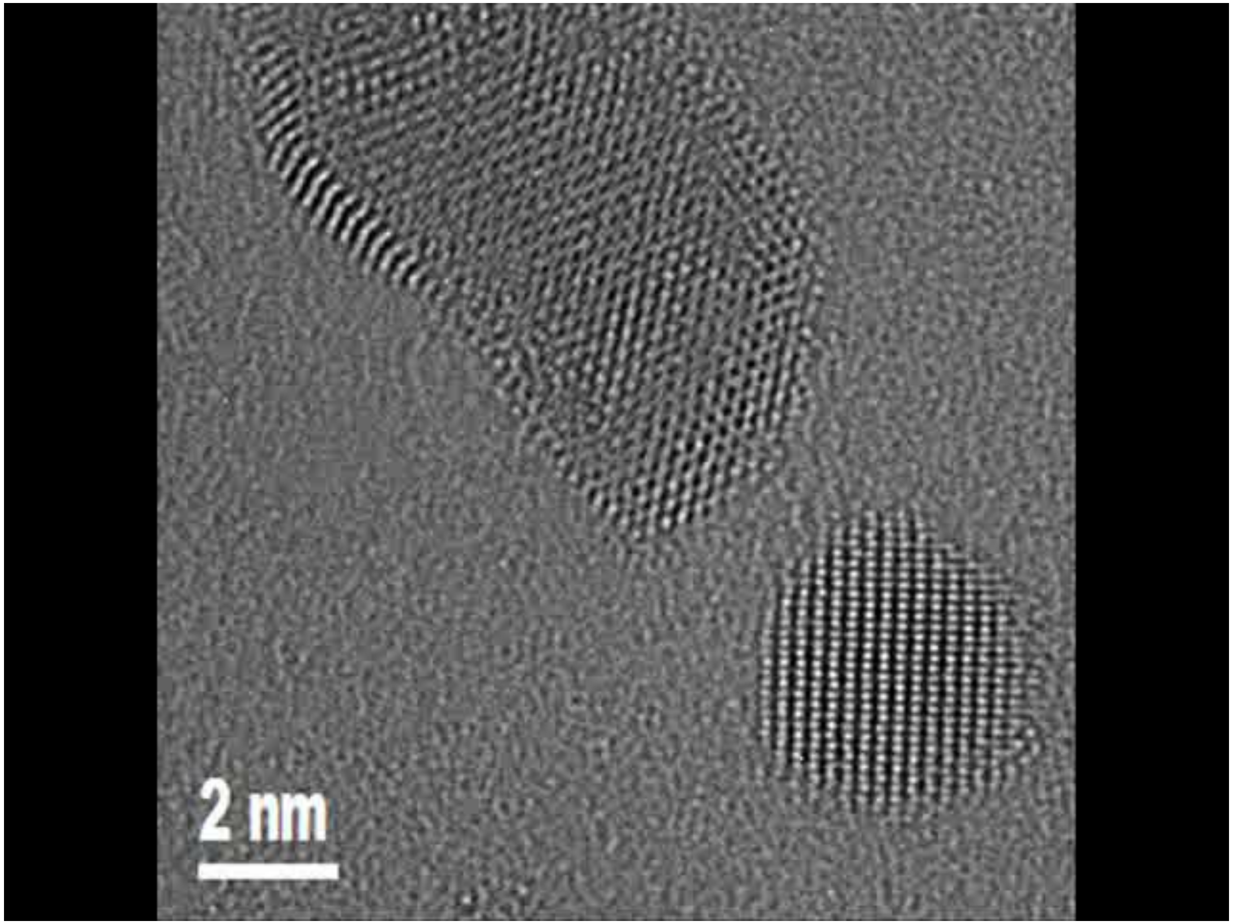
$$\bar{R}_{shrink}(38\ nm) < \bar{R}_{Grow}(57\ nm)$$

But 20% of the NPs that shrink have a radius > $\bar{R}_{Grow}$

Ostwald ripening is not only driven by size effects

Khelfa et al. Advanced Materials 33, 2102514 (2021)

Growth mecansisms : Coalescence



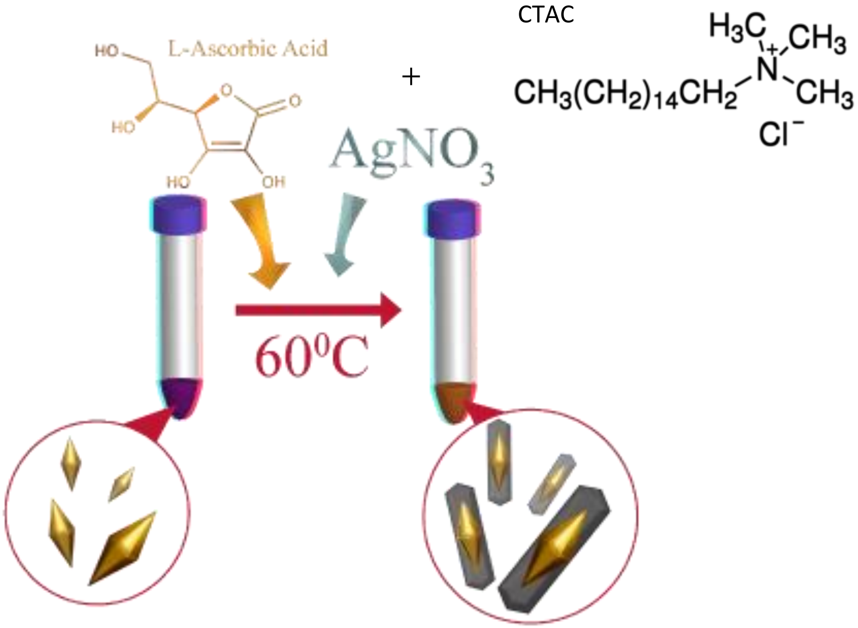
Oriented attachment to minimize the interface energy !

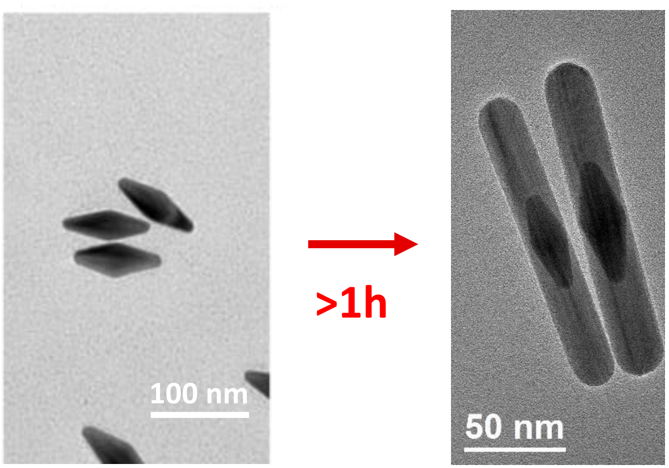
Can LPTEM experiments be compared with bench scale synthesis ?

From nanoscale
***in situ* observations…**

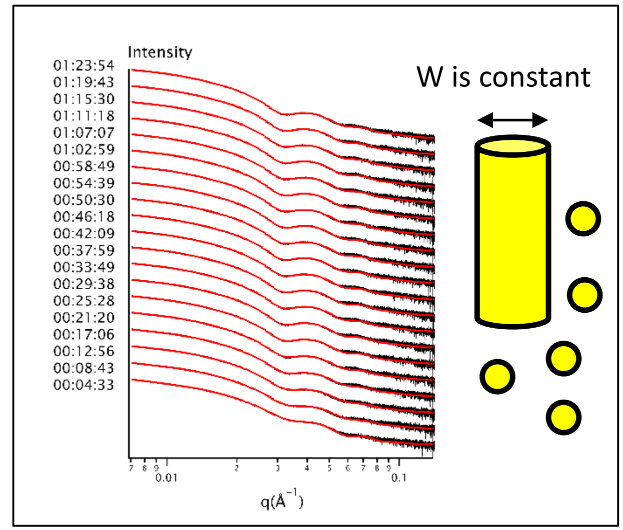
…to bench-scale synthesis

Towards multi-modal in situ approach

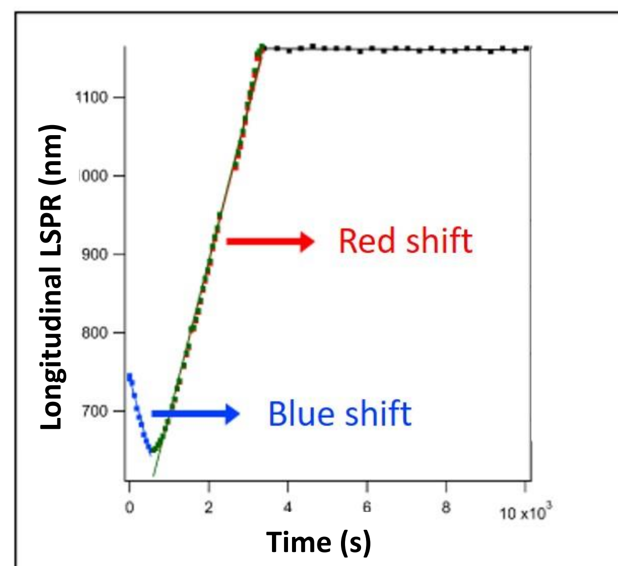




Real-time SAXS (SOLEIL Synchrotron)

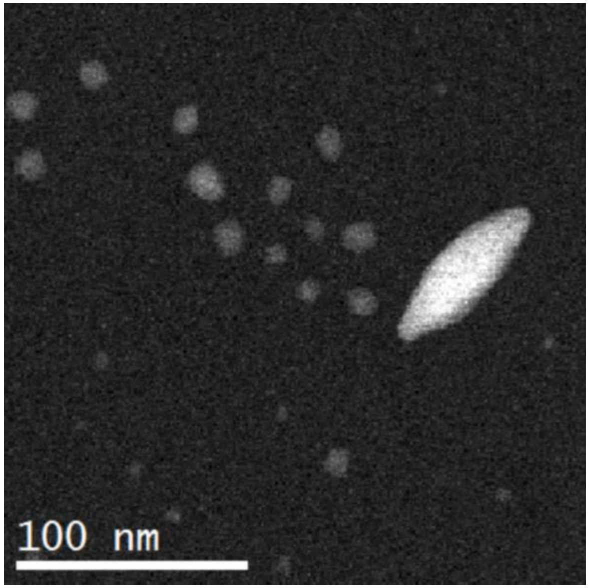


Real-time absorption spectroscopy

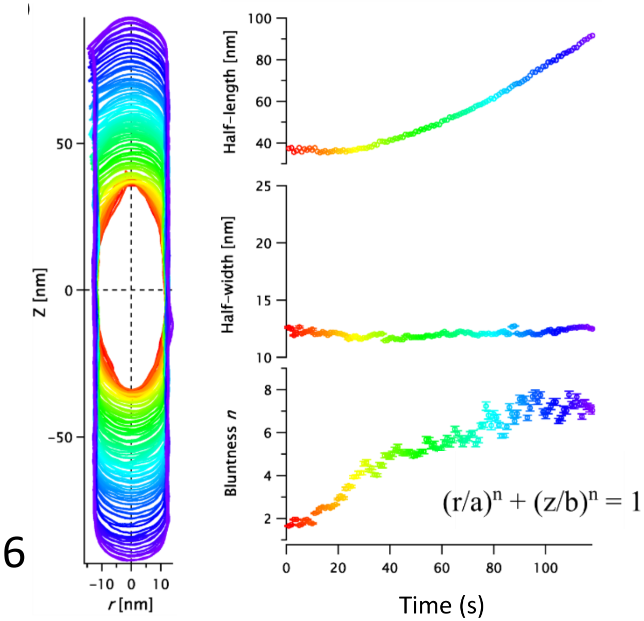


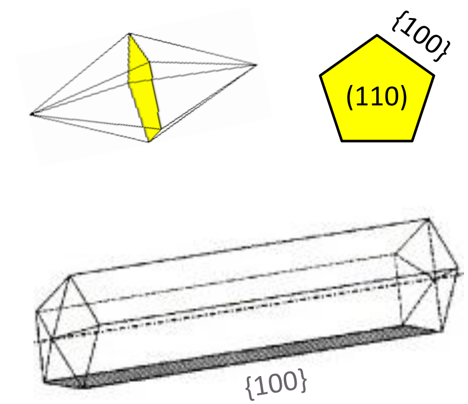
Collaboration with Cyrille Hamon & Doru Constantin (LPS, Paris Saclay University)

Visualize intermediate structures and reaction dynamics

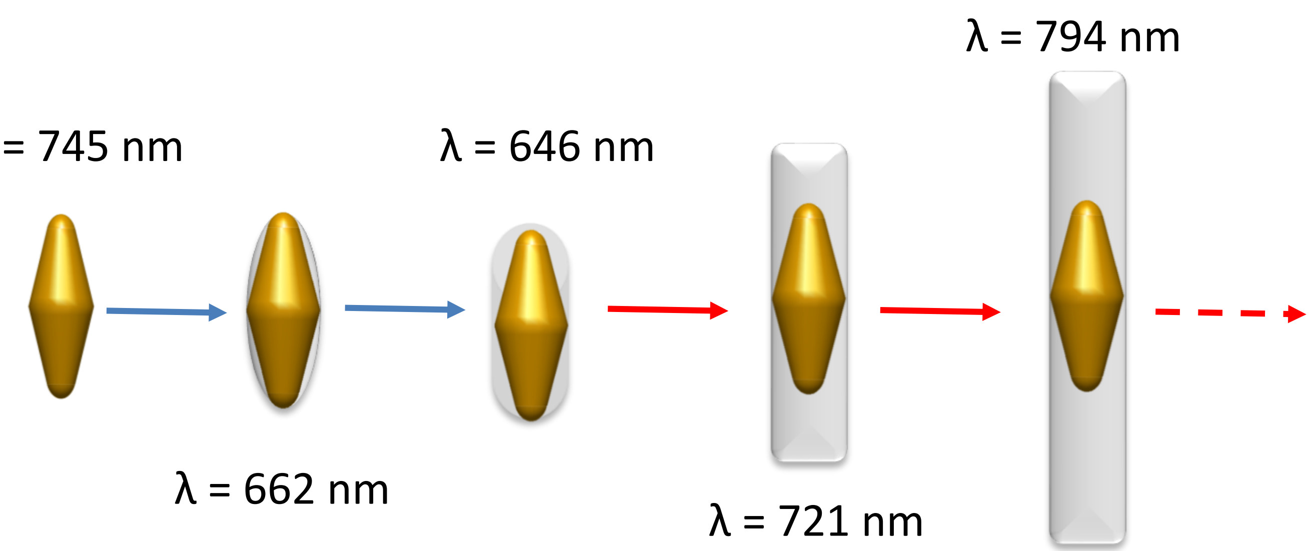


x16





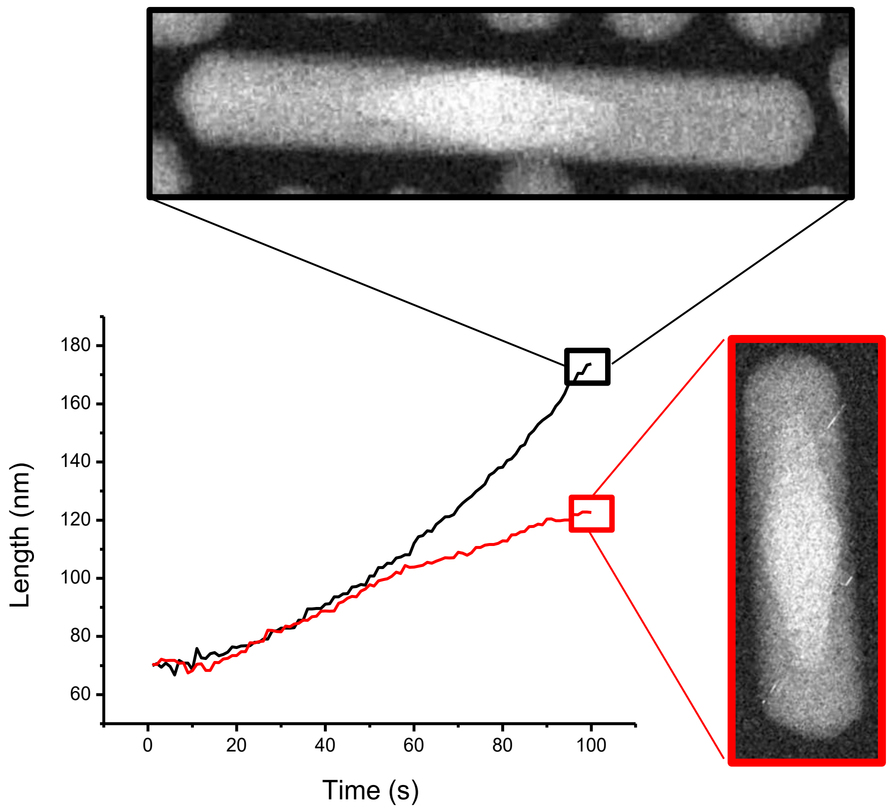
BEM Simulations of LSPR



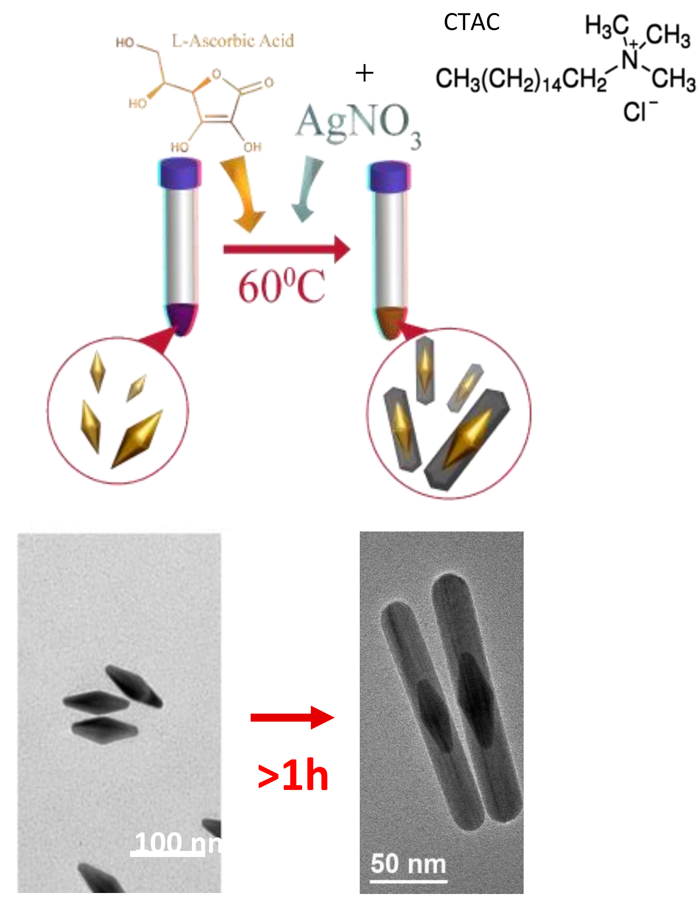
Aliyah et al. J. Phys. Chem. Lett. 11 2830 (2020)

Multi-scale investigations of the growth processes

Synthesis in the TEM



Bench-scale synthesis

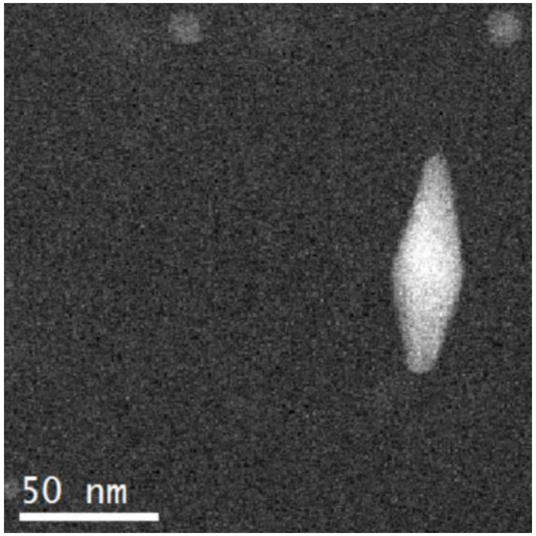


Anisotropic growth is governed by thermodynamic effects

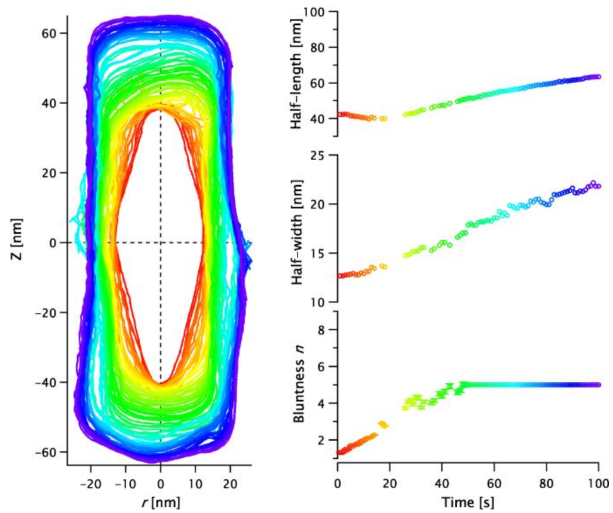
Aliyah et al. J. Phys. Chem. Letters 11, 2830 (2020)

Reveal the role of each chemical in the synthesis

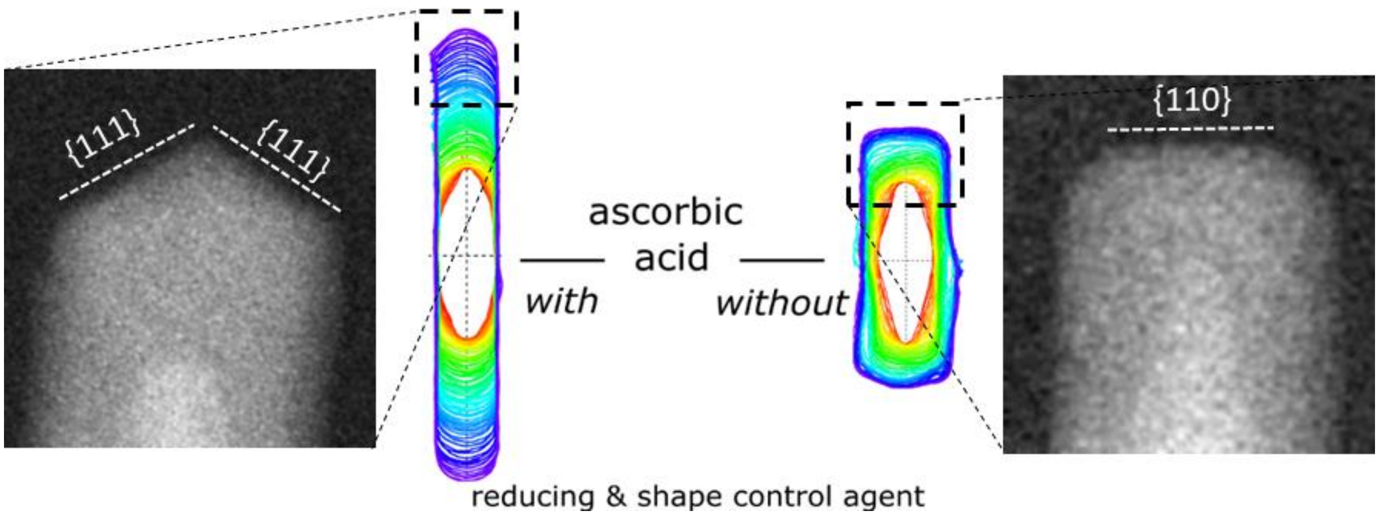
Without ascorbic acid



x8

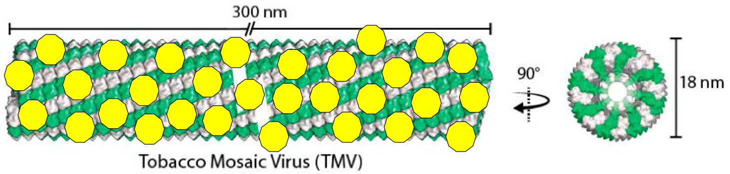


Ascorbic acid is not only a source of electron but it is also shape directing agent !



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

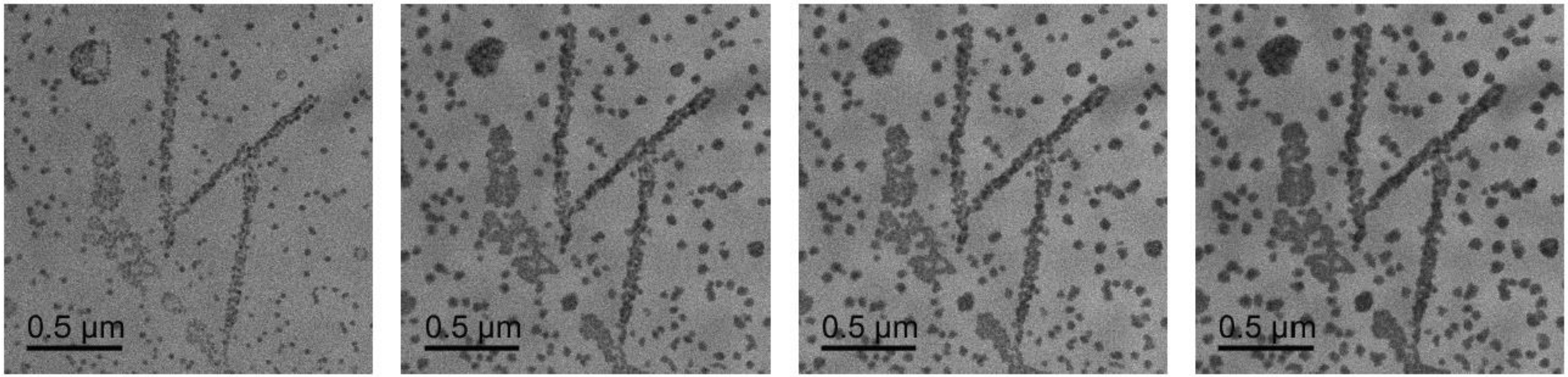
Biotemplated synthesis of gold NPs on TMV virus



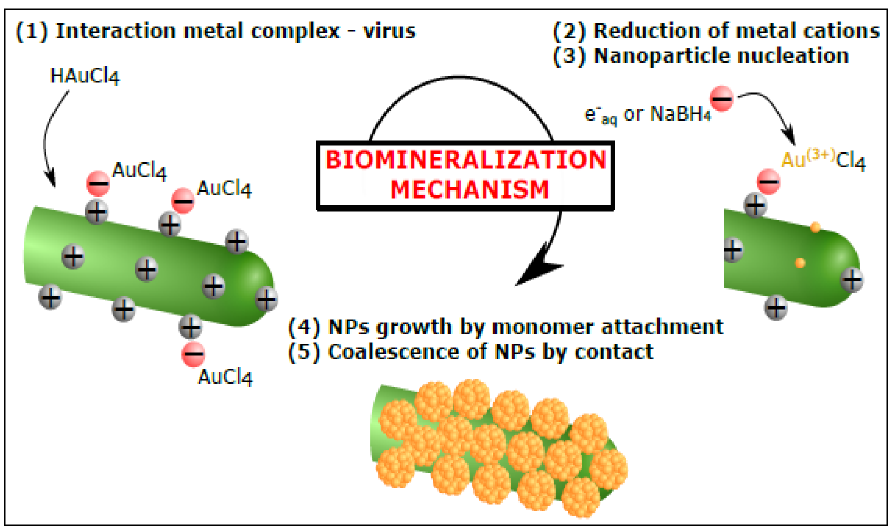
How to increase the density of gold NPs at the surface of TMV ?

ITODYS
Cora Moreira da Silva
Thanh Ha Duong

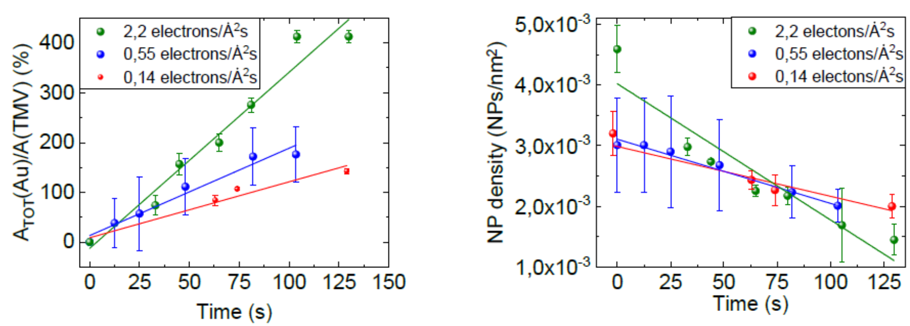
Rationalizing Biotemplated synthesis



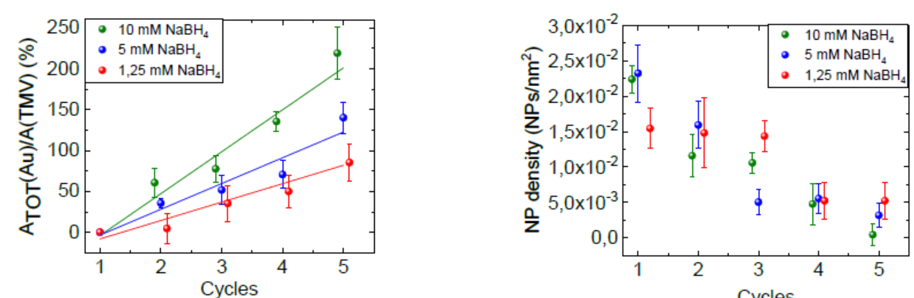
(a) $t = 0$ s (b) $t = 63$ s (c) $t = 74$ s (d) $t = 129$ s



In situ TEM synthesis

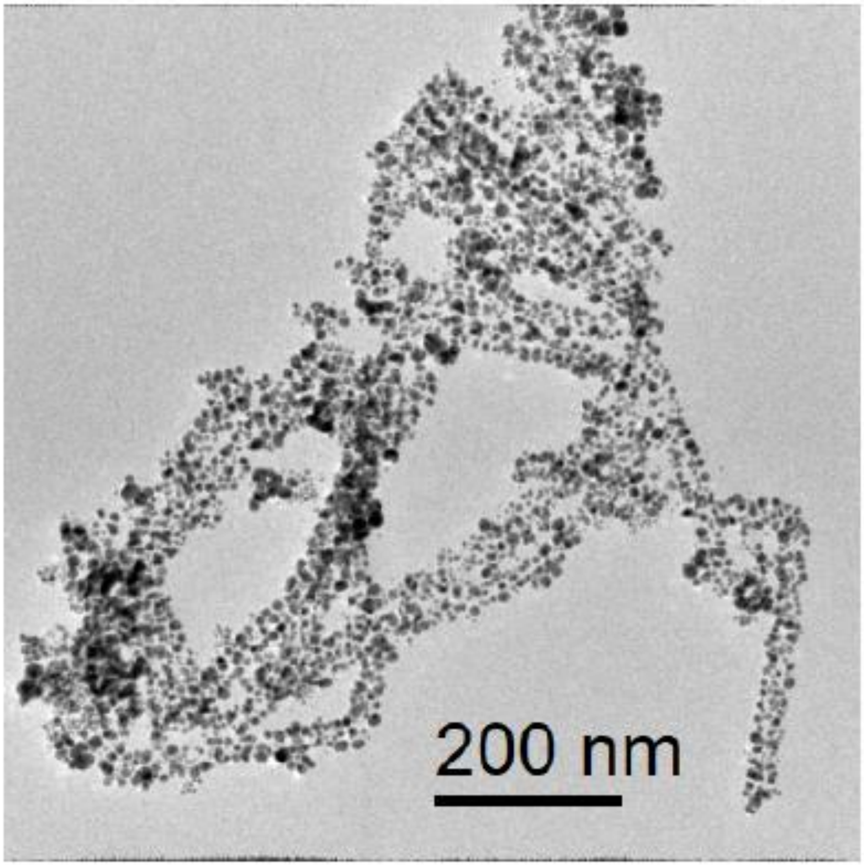


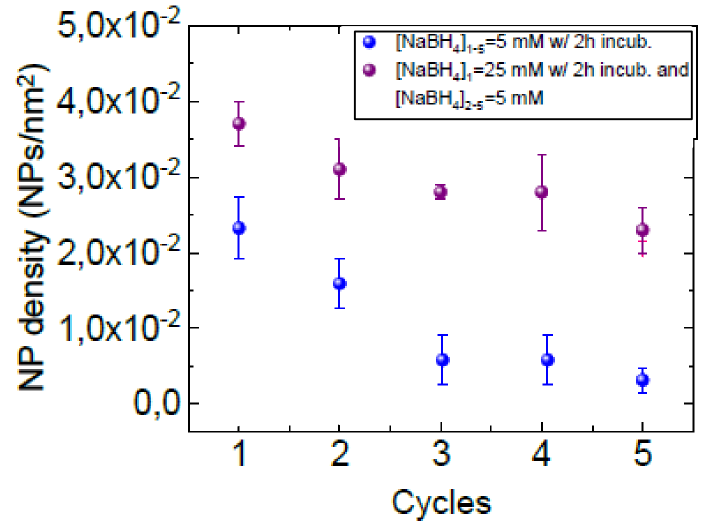
Bench scale synthesis

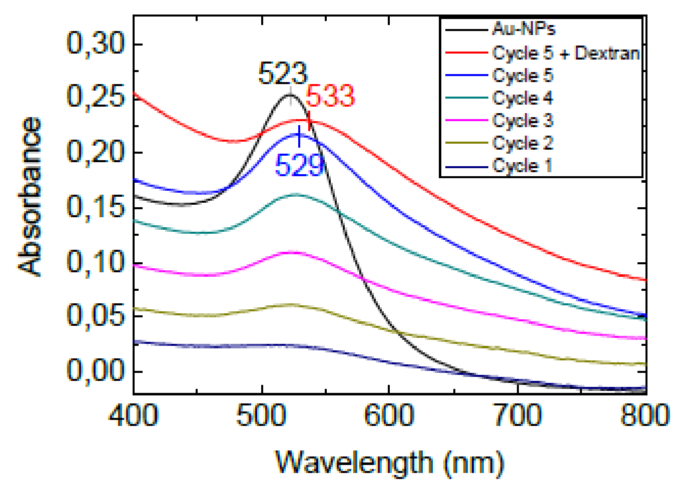


Moreira Da silva et al. Nanoletters 23, 5281 (2023)

Rationalizing Biotemplated synthesis



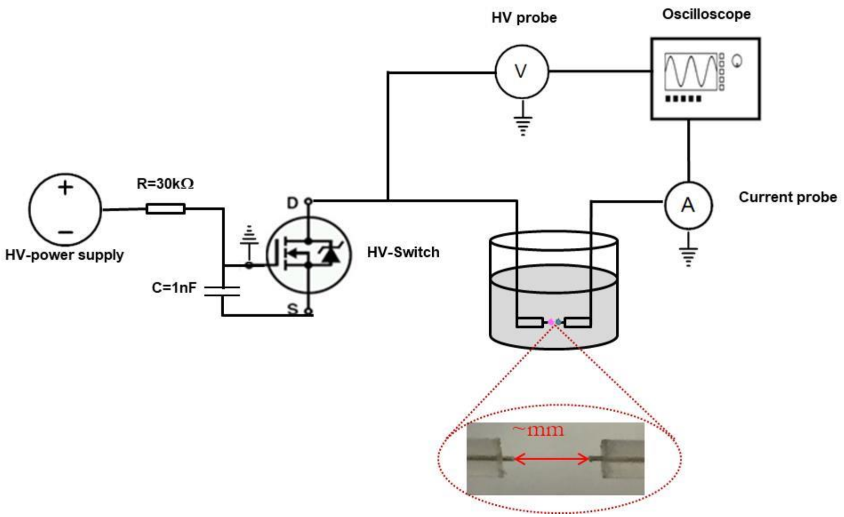




Bench-scale synthesis:
Viruses decorated with a higher density of NPs

Moreira Da silva et al. Nanoletters 23, 5281 (2023)

Can LPTEM experiments be compared with plasma driven synthesis ?



Large scale and clean synthesis processes !

Pulsed plasma discharge in water

Excitation, ionization and dissociation of water molecules by electron impact

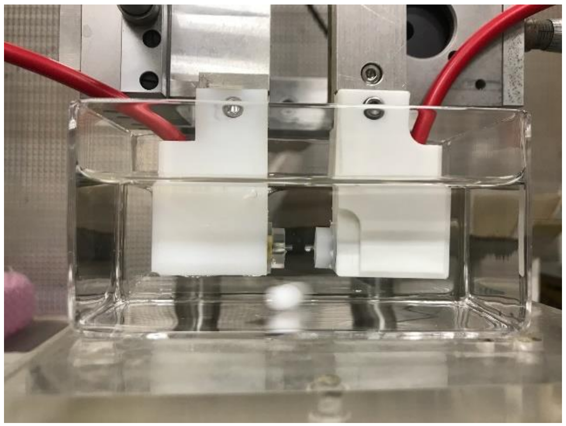
$OH^{\bullet}$,$H^{\bullet}$,H_2O^+,e-,H_3O^+,(e_{aq}^-),H_2O_2,O_2,H_2
(same reactive species than in the electron beam driven rodiolysis of water)

Collaboration with Arlette Vega Gonzalez (LSPM, Université Sorbonne Paris Nord)

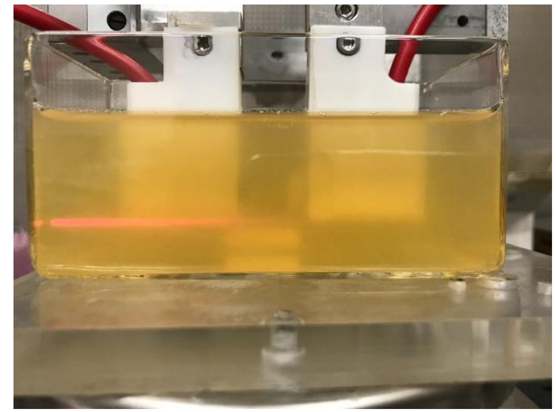
Synthesis of iron oxyde nanoparticles by PLI synthesis

Précursors : $(NH_4)_2Fe(SO_4)_2$

pH =3-4



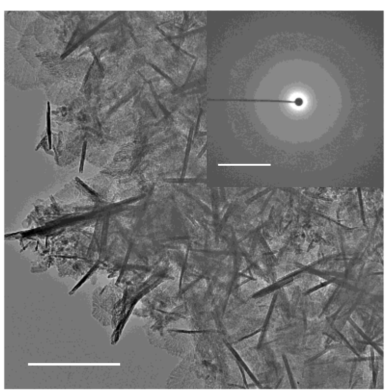
Plasma 10 kV



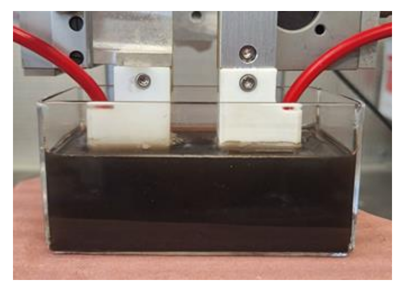
No crystaline nanostructures

pH =11

Amorphous $Fe(OH)_2$



Plasma 10 kV

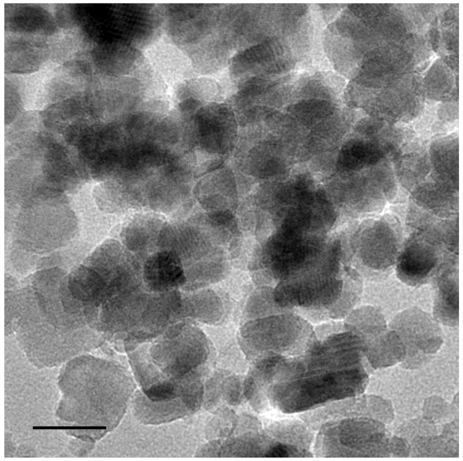


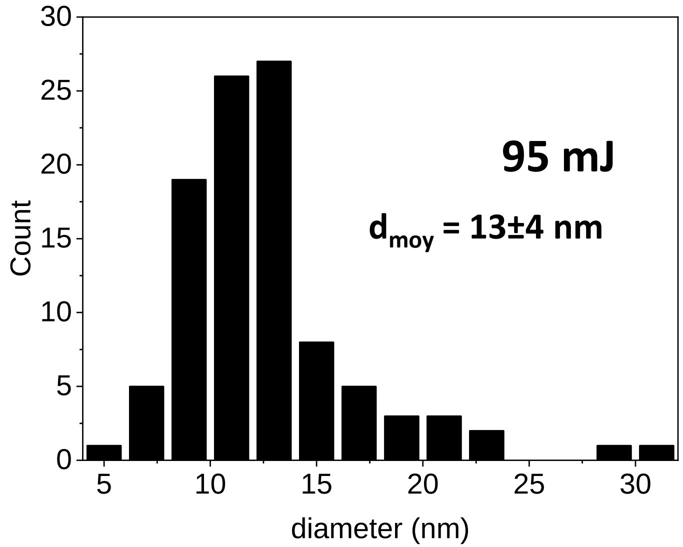
Magnetic colloids

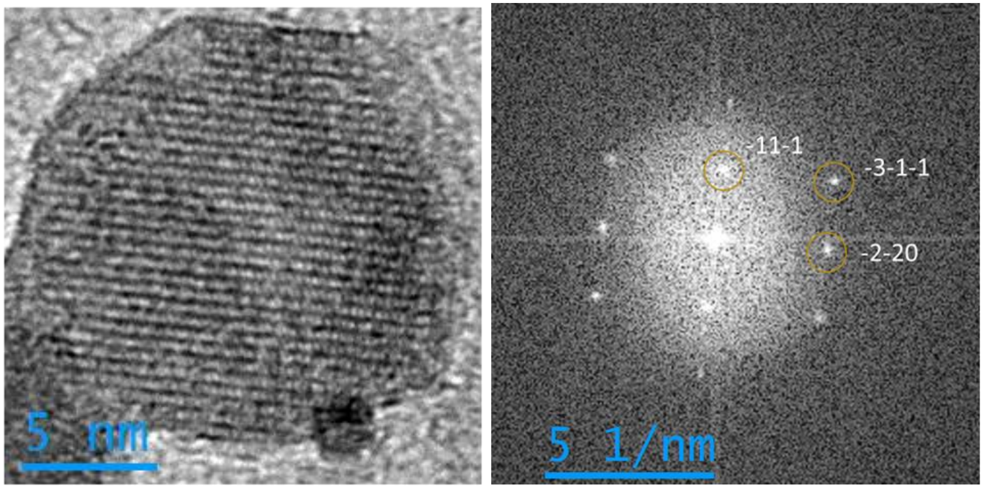
T. Blin et al in preparation

Synthesis of iron oxyde nanoparticles by PLI synthesis

95 mJ (10kV)





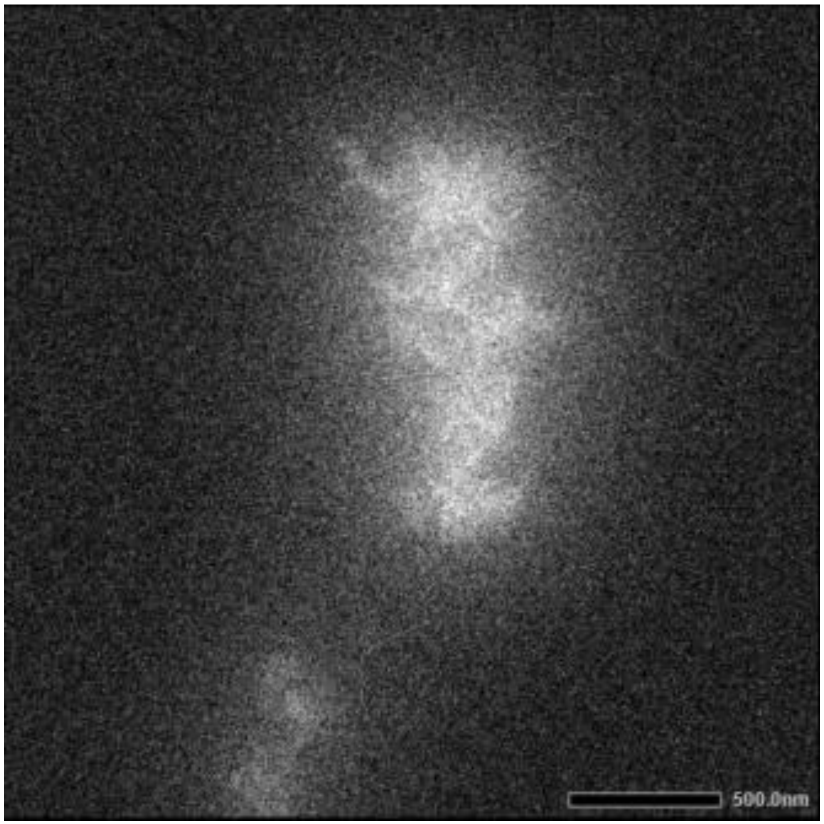


Inverse spinel structure : **γ-Fe_2O_3 or Fe_3O_4**

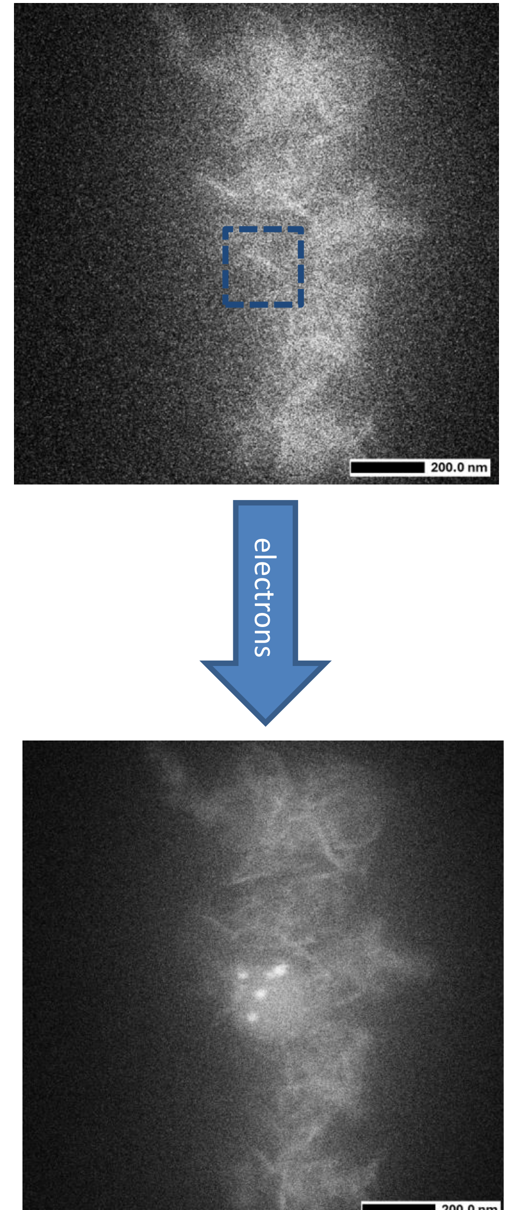
T. Blin et al in preparation

Iron oxyde nanoparticles formation driven by radiolysis

in situ TEM Conditions : $(NH_4)_2Fe(SO_4)_2$ à 1 mM, pH 10-12



x10



3 FeO(OH)+ e^{-}_{aq} + $OH^{\cdot}$ → Fe_3O_4 + H_2O + $2OH^{-}$ [2014, Ekoko]

Thank you

Jaysen Nelayah
Christian Ricolleau
Guillaume Wang
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Abdelali Khelfa
Abdallah Nassereddine
Hakim Amara
Syrine Krouna
Adrien Momcomble
Vinavadini Ramnarai
Thomas Blin

Cyrille Hamon
Daru Constantin
Claire Goldmann

Arlette Vega Gonzalez

Cora Moreira da Silva
Thanh Ha Duong
Frederic Kanoufi
Jean Marc Noel
Jean Francois Lemineur

Foundings :

Save the date !!