Synthèse de nanoparticules par ablation laser : principes – exemples – applications

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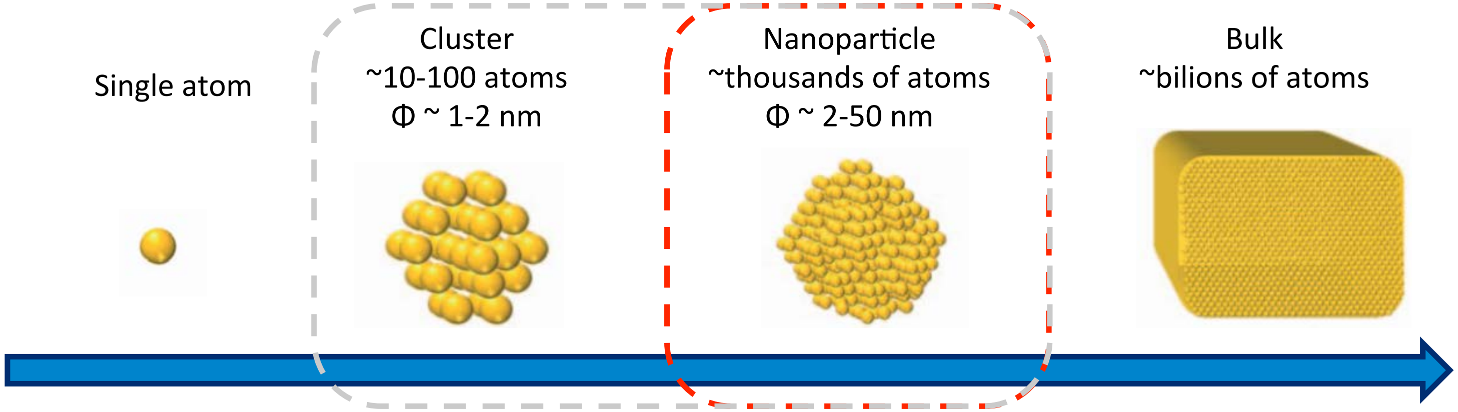
Introduction to nanoparticles

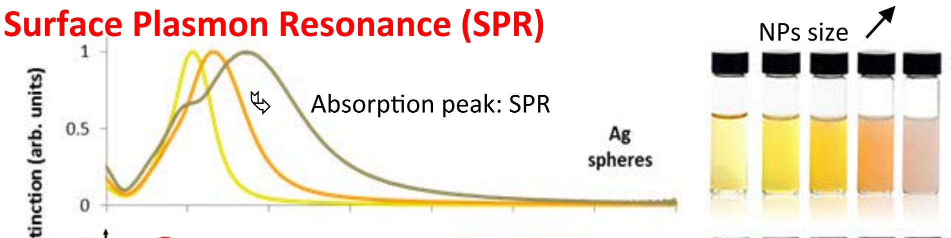
Properties versus scales

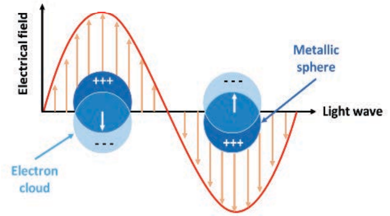
- Different properties at different scales



- Discrete electronic level vs Electronic band structure

Metal. NPs
Surface Plasmon Resonance (SPR)

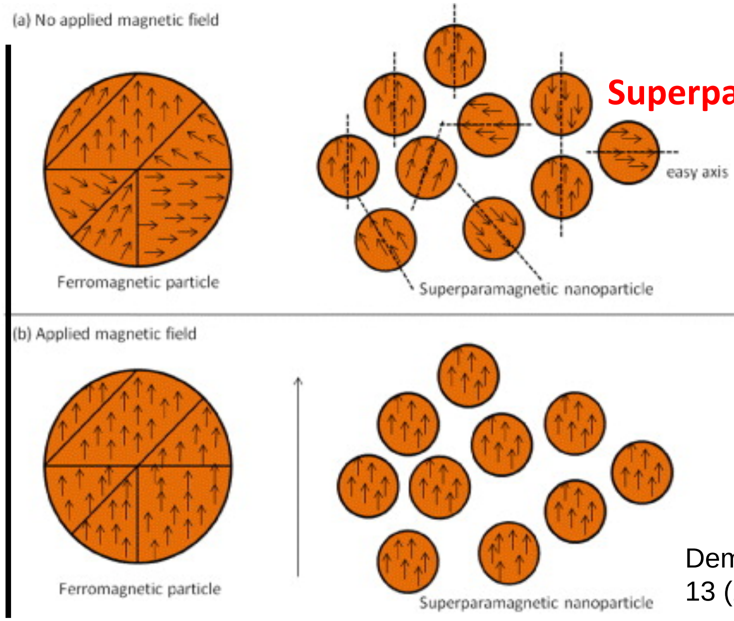




Resonant oscillation of conduction e- stimulated by E

Oldenburg, Proc. SPIE 4810, Properties of Metal Nanostructures, 36 (2002)

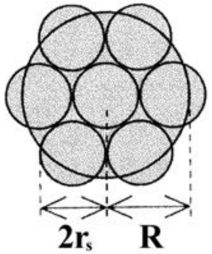
Oxide NPs
Superparamagnetism



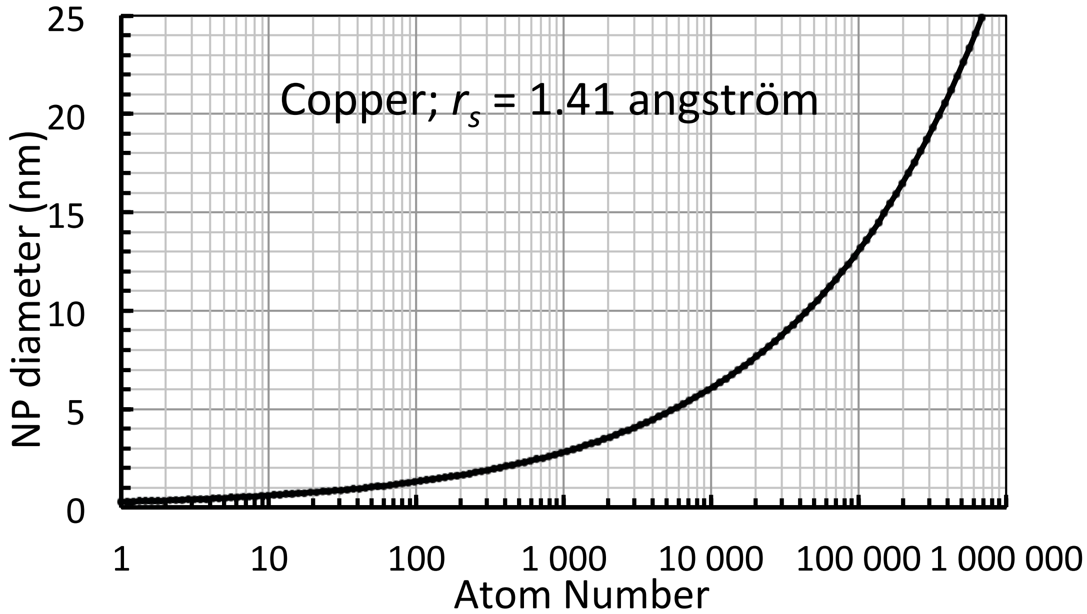
Demas, New J. Phys. 13 (2011)

Some numbers

Hyp: spherical NP constituted by *n* atoms
r_s Wigner-Seitz atomic radius



$$R = r_s \, . \, n^{(1/3)}$$



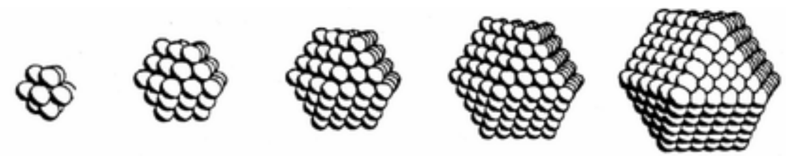
Diameters

- ✓ 1 nm ≈ 45 atoms
- ✓ 3 nm ≈ 1 272 atoms
- ✓ 5 nm ≈ 5 844 atoms
- ✓ 10 nm ≈ 43 249 atoms

Ratio R $$R = \frac{\text{Surface atoms}}{\text{Number of atoms in cluster}}$$

Atoms number →	13	55	147	309	561 (2.3 nm Ø)

(*)



Number of shells	1	2	3	4	5
Number of atoms in cluster	M_{13}	M_{55}	M_{147}	M_{309}	M_{561}
Percentage surface atoms	92%	76%	63%	52%	45%

(*) G. Schmid, Endeavour, Cluster and Colloids – Bridges Between Molecular and Condensed Material, **14** (1990)
Aiken J. Mol. Catal. A: Chem. **145** (1999)

Homogeneus nucleation; vapor phase

Thermodynamic Approach

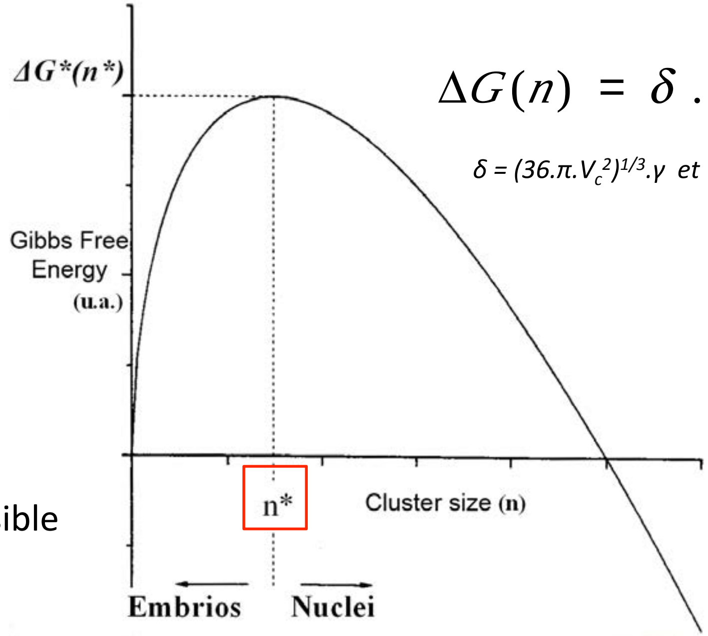
Free energy change

$$\Delta G(r) = 4 . \pi . r^2 . \gamma + \frac{4}{3} . \pi . r^3 . \Delta G_v$$

Surface free energy vs Volume free energy

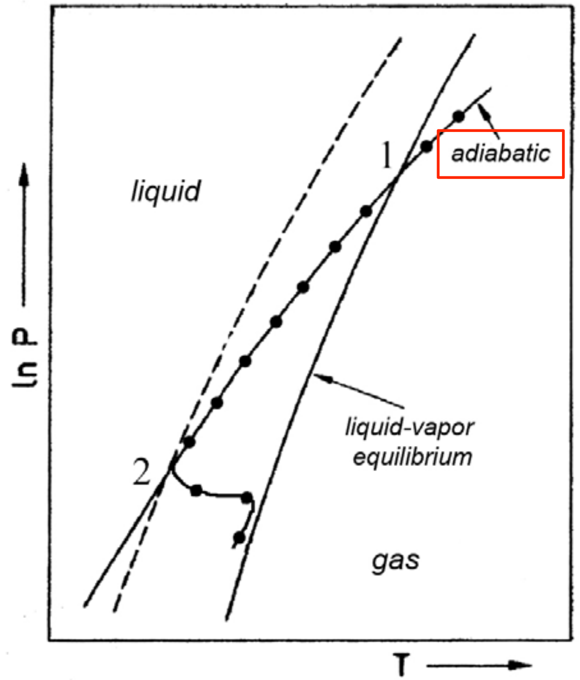
$$\Delta G_v = -\frac{k.T}{V_C} . \ln \frac{P}{P_s}$$

- *S > 1* : Sursatured vapor; Spontaneus nucleation possible
- *S < 1* : just vaporisation



$$\Delta G(n) = \delta . n^{\frac{2}{3}} - k.T. \ln S . n$$

$\delta = (36.\pi.V_c^2)^{1/3}.\gamma$ et $k.T.\ln S = \Delta\mu$ chemical potential
k: Boltzman Constante
T: nucleation Temprature
S: sursaturation rate



Sursaturation needed
S = P / Ps

- *P* vapor partial pressure, *Ps* saturated vapor pressure @ *Ts*
- *Ts* interface Temperature

adiabatique expansion

Sursaturation conditions → gas under high pressure (He, thermal conductivity)

↳ surpersonic beam
↳ specific process

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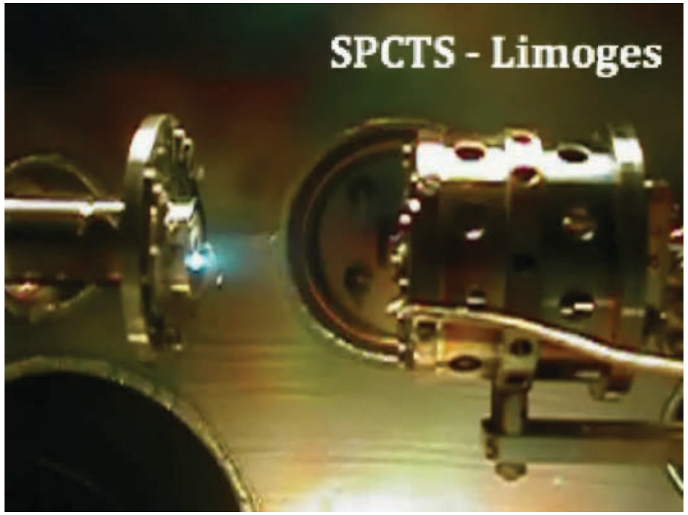
Laser vaporisation sources: principle



History – Smalley source

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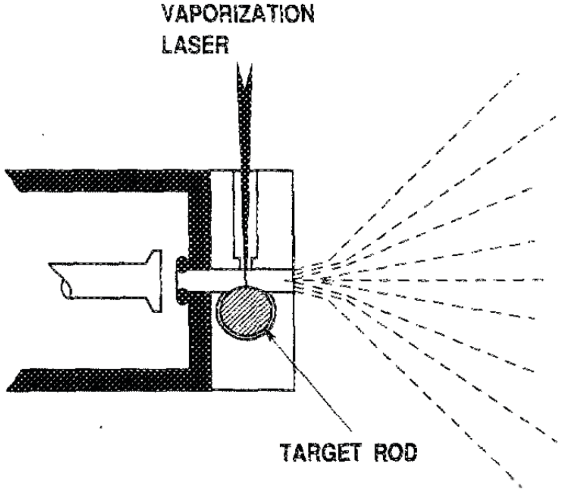
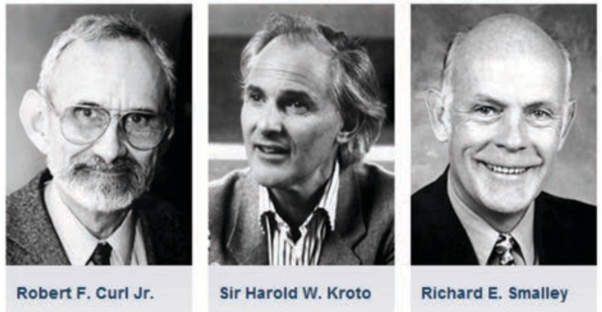
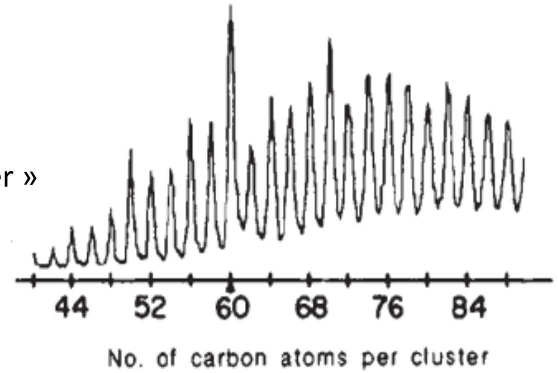
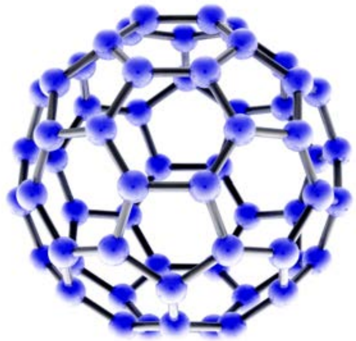




1996 Nobel Prize in Chemistry

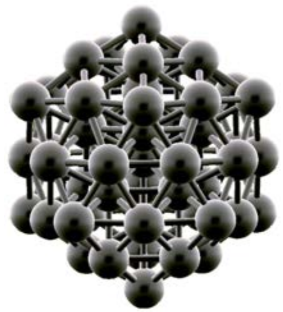
- « Magic number »





NP composed of 60 Carbon Atoms (C_{60} fulleren – Bucky Ball)

- Remark:



Ag Dense NP composed of 55 Silver Atoms

[1]R.E. Smalley et al., J. Chem. Phys. 74(11) (1981)
[2]R.E. Smalley, Laser Chem. 2 (1983)
[3]H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, "C60: Buckminsterfullerene", Nature 318 (1985)

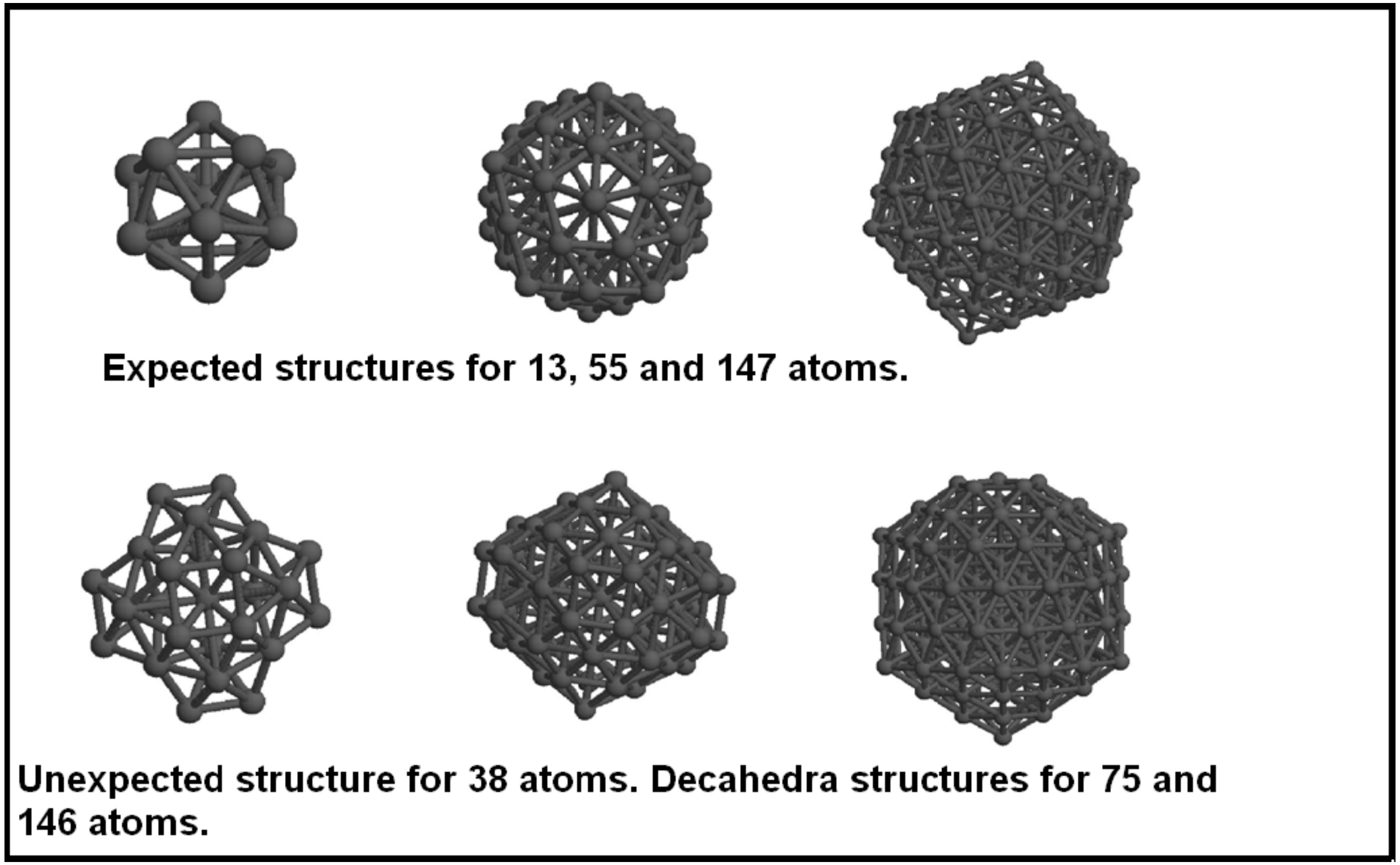
Cluster: Magic number

Molecular dynamics simulation, growth process of isolated Co clusters in gas phase

icosahedral

Structures

D4h symmetry



truncated icosahedral

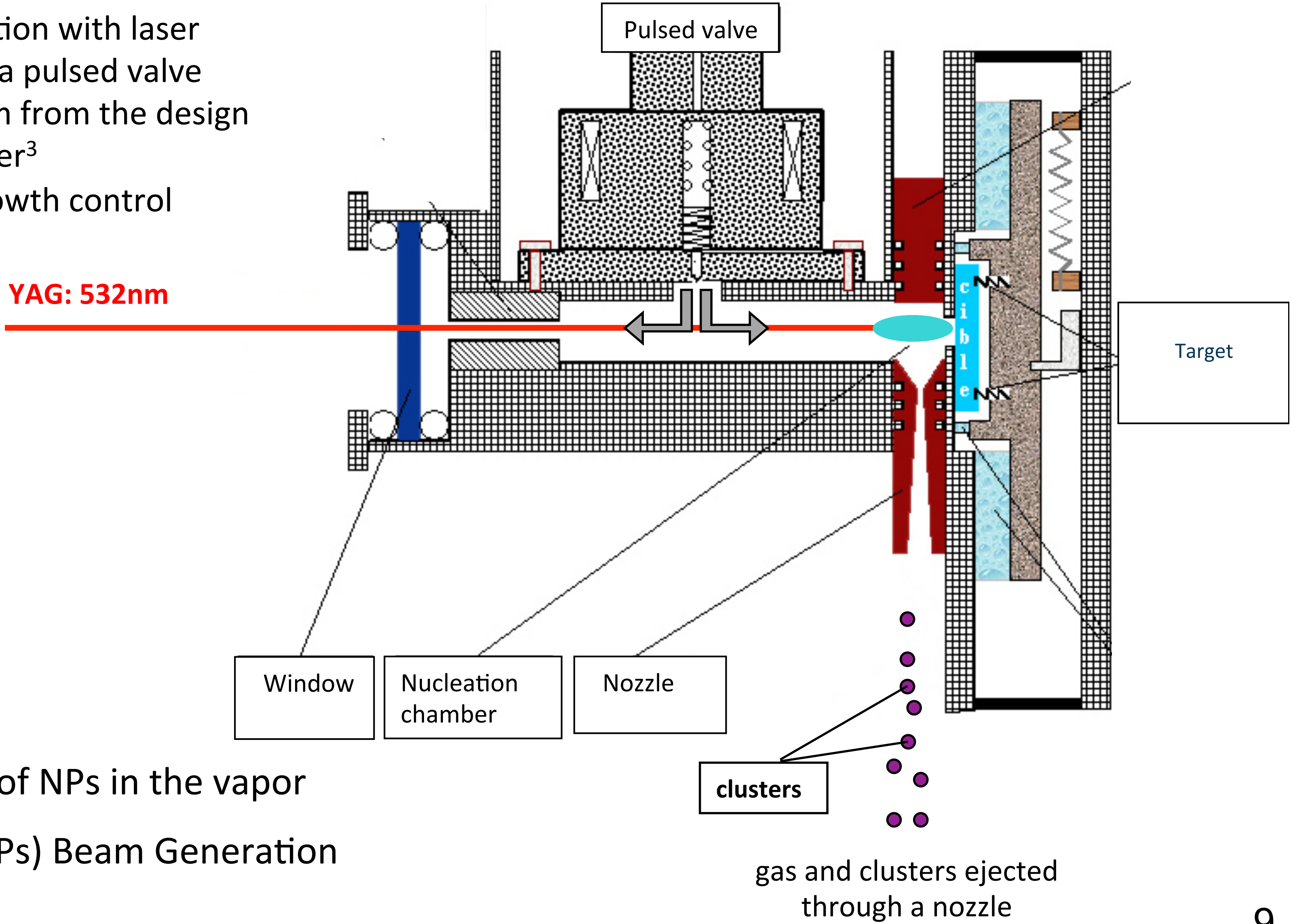
Principle:

Cluster Beam Generator (CBG);
Laser Vaporisation Sources (LVS); Free Cluster Generator (FCG)

Principle :

Target vaporization with laser
Gas injected by a pulsed valve
Nucleation room from the design of Milani-De Heer[3]

↳ Clusters growth control

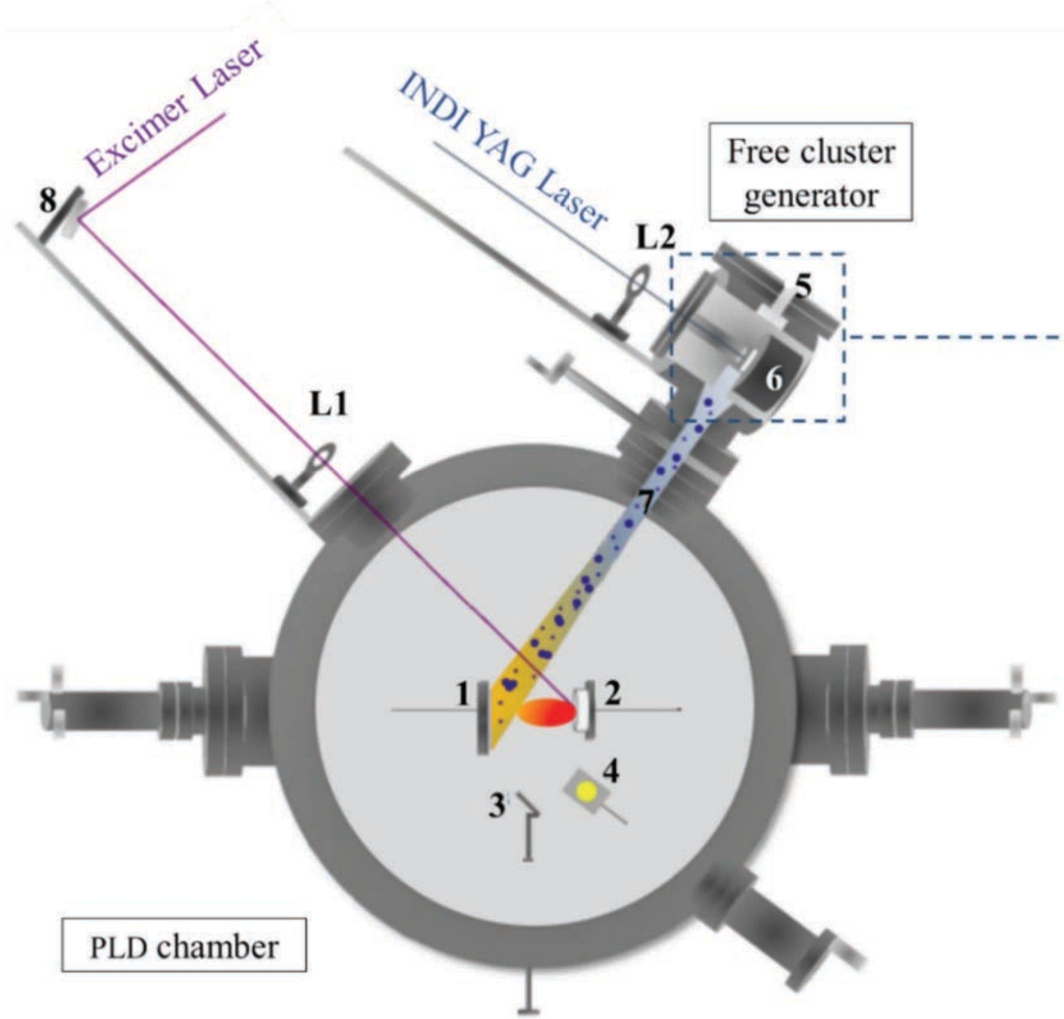


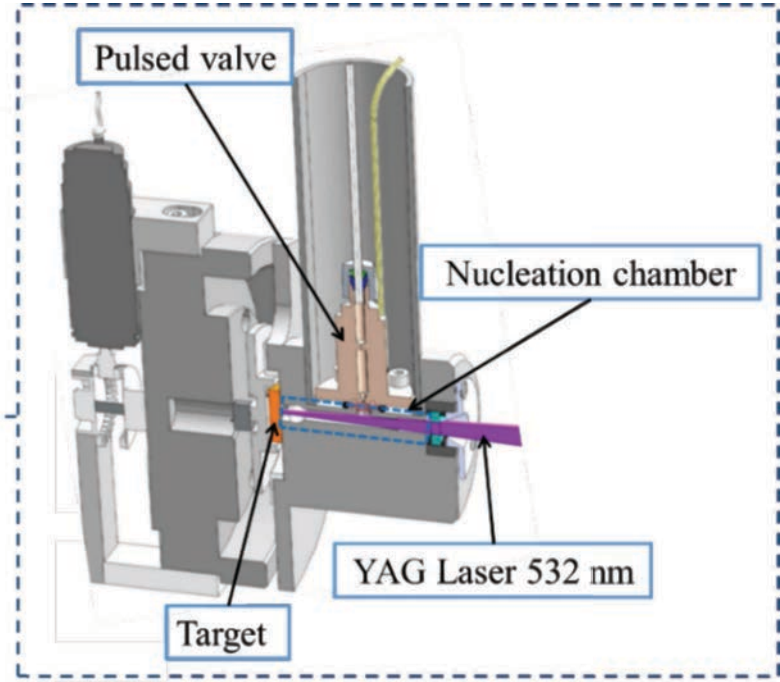
↳ synthesis of NPs in the vapor

↳ cluster (NPs) Beam Generation

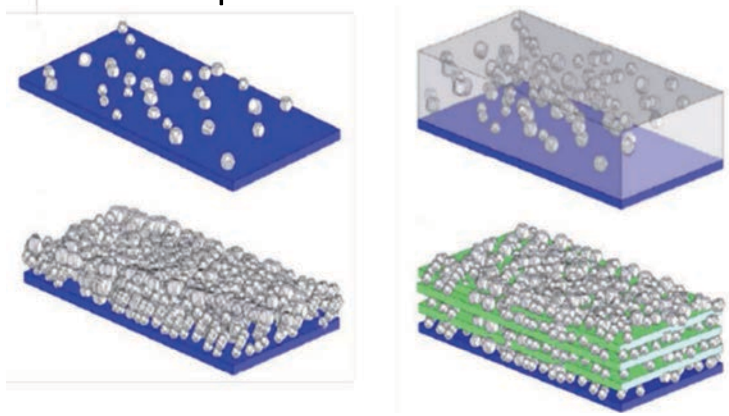
[3]P. Milani, W.A. deHeer, Rev. Sci. Instrum. 61 (1990)

NP Beam Generator (home made)





Deposition modes



Combined matrix & NPs properties / NPs scale effect

[1]*Gaudin, Constantinescu, Champeaux, Dumas-Bouchiat « A dual pulsed laser set-up for the synthesis of nano-sized clusters »*, submitted

Limoges laser vaporisation source

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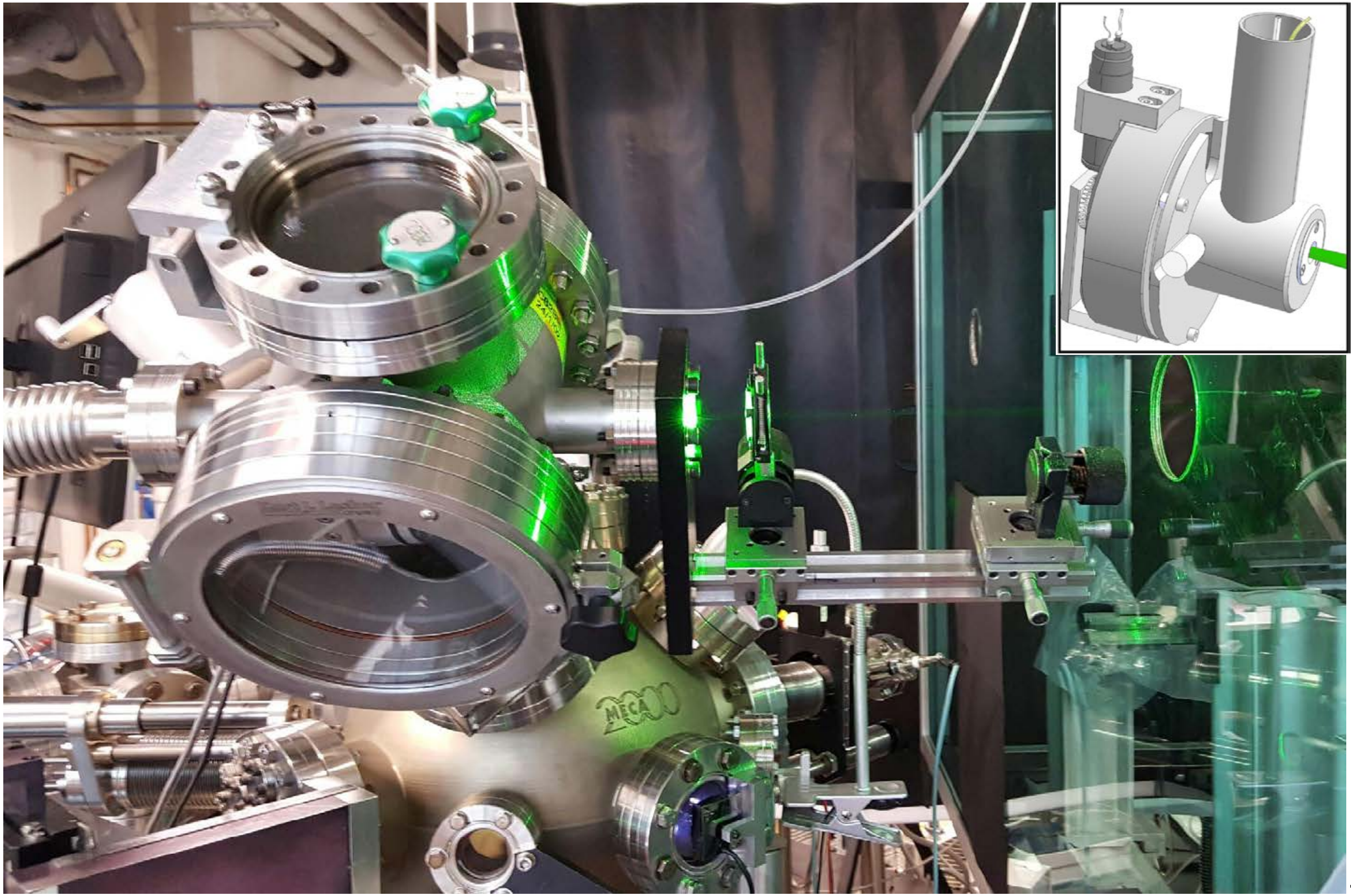
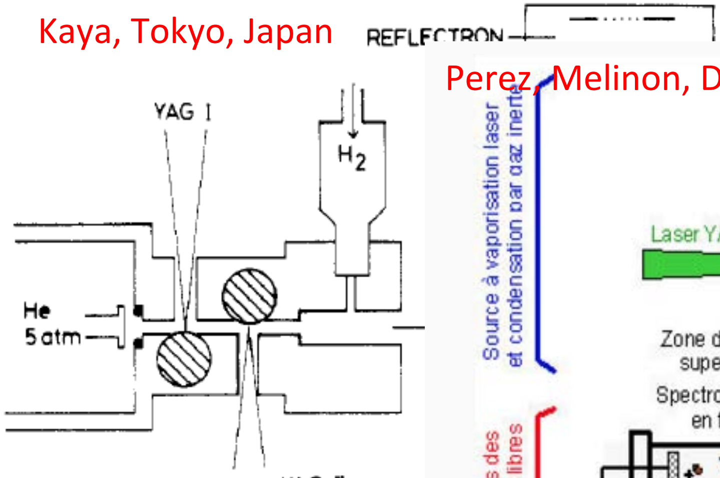
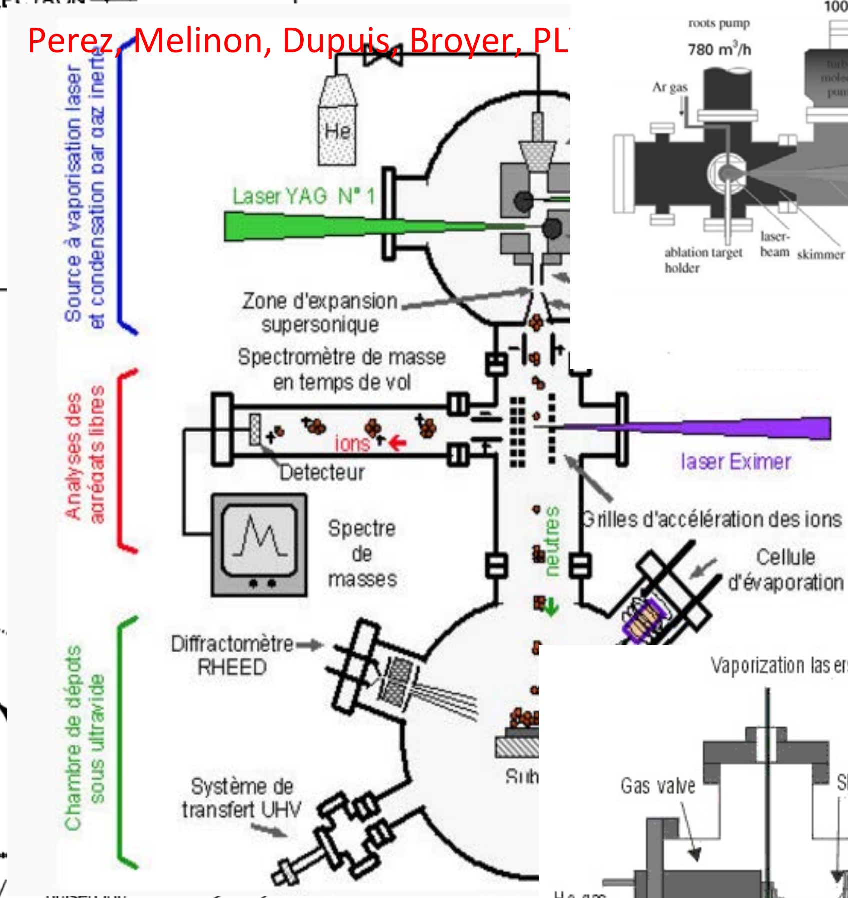


Smalley's childs

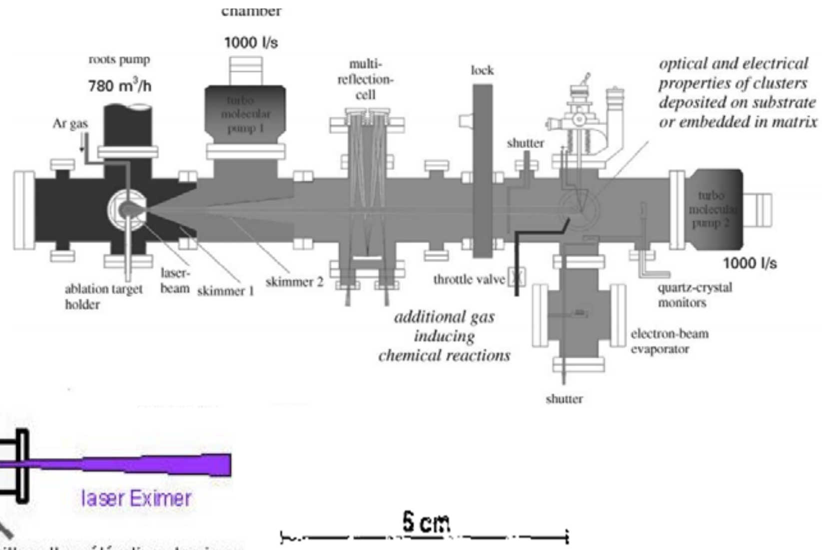
Kaya, Tokyo, Japan



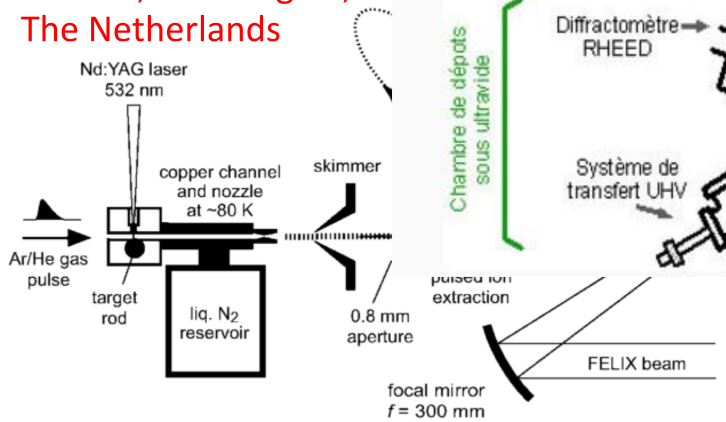
Perez, Melinon, Dupuis, Broyer, PL



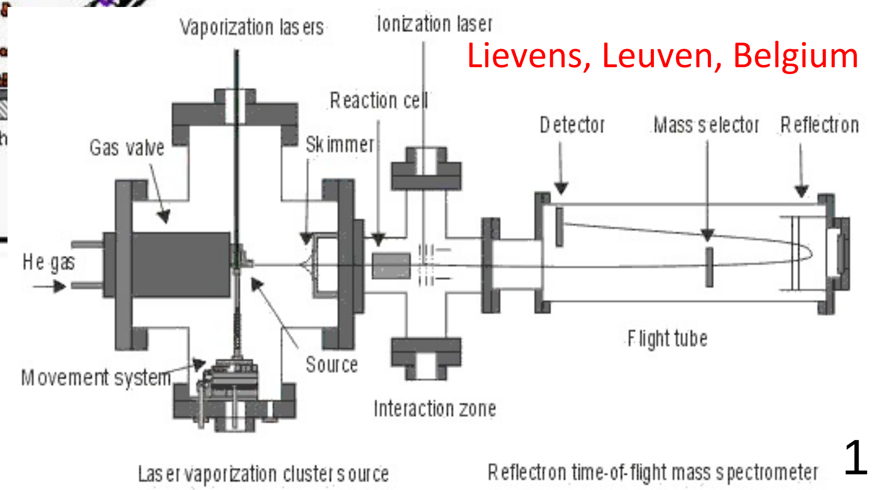
Kreibig, Aachen, Germany



Fielicke, Nieuwegein, The Netherlands

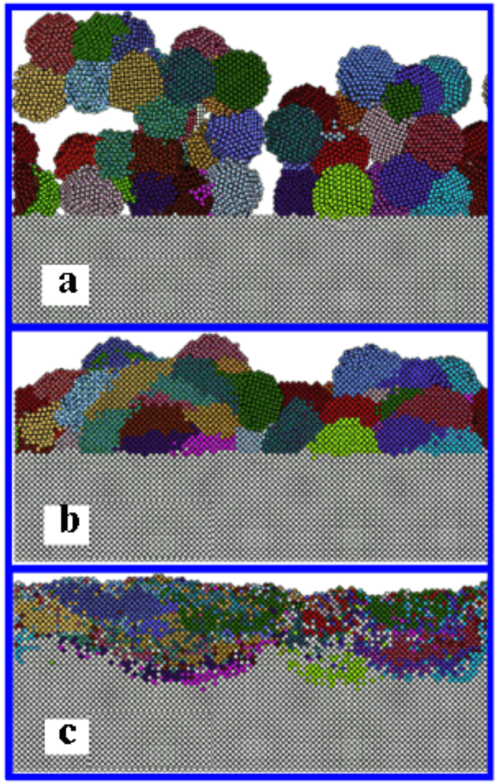


Lievens, Leuven, Belgium



Low Energy Cluster Beam Deposition (LECBD)

Modelling from Haberland et al. Mo NPs stacks on Mo substrate[1]



➯ **Cluster @ 0,1 eV/at:**
keep their flying characteristics
Highly porous stacks of NPs (~50%)[2]
Weak adherence

➯ **Probability of NP fragmentation is weak**

➯ **Cluster @ 1 eV/at:**

➯ **Clusters @ 10 eV/at:**

Dense « epitaxial » (Mo on Mo-substrate)

[1]Haberland, Phys. Rev. B 51 (1995)

Approximation, overestimated cluster velocity :
NP velocity V_{max} ≈ gas velocity $V_{échappement}$ (sound velocity v_∞)

$$v_\infty = \frac{2k}{m_{H_e}}\left(\frac{\gamma}{\gamma-1}\right)T = 1700\text{m/s (He)}$$

Cobalt NP :
Kinetic-E ≈ 0.7 eV/at
Cohesion-E (bulk) ≈ 4.5 eV/at → $E_{cinétique} << E_{cohésion}$ ➯ **NP keep their flying shape (shape memory)**

[2]Dumas-Bouchiat, J. Appl. Phys. 100 (2006)

NP growth: homogeneous nucleation theory

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Kinetic equations for NP-NP reactions:

$$\frac{dn_k^*}{d\tau(t)} = \underbrace{\sum_{\substack{i+j=k \\ i\le j}} C_{ij}^* . n_i^* . n_j^*}_{\text{Formation rate of k-sized NP resulting from the coalescence of a i-NP and a j-NP}} - \underbrace{\sum_i C_{ik}^* . n_i^* . n_k^*}_{\text{Number of events where k-sized NPs form bigger NPs}}$$

C_{ij}: coalescence probability between a i-NP and a j-NP

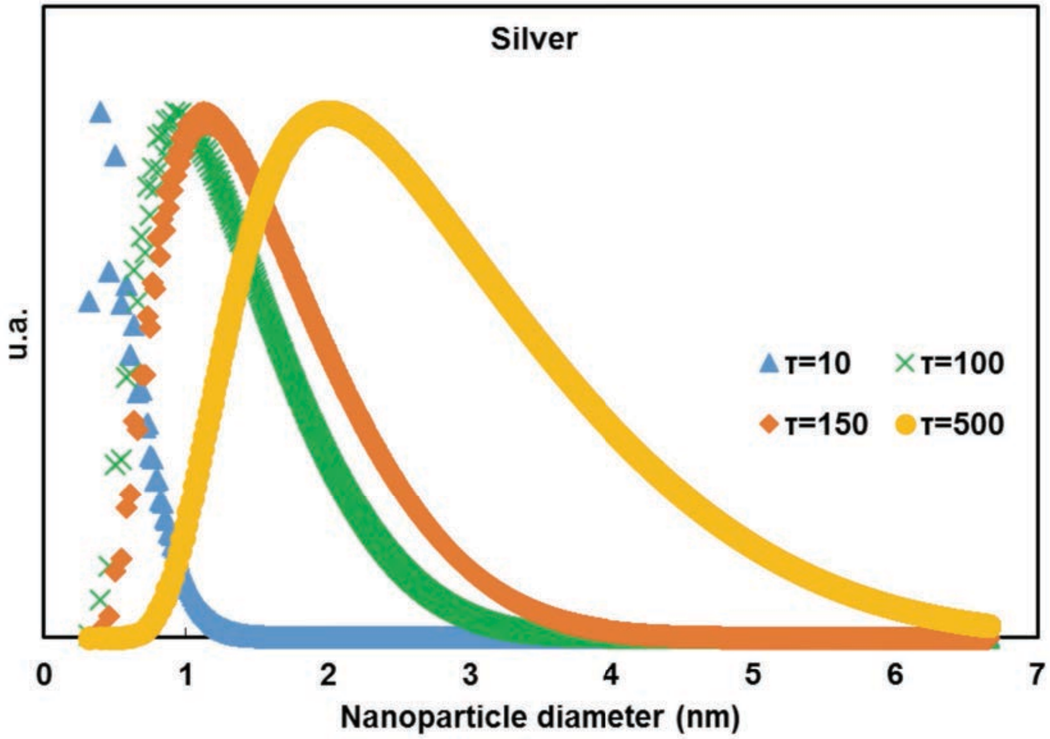
$n_i^* = \frac{N_i}{N}$ reduced variable

n^*_i: number of i-sized NPs

n^*j: number of j-sized NPs

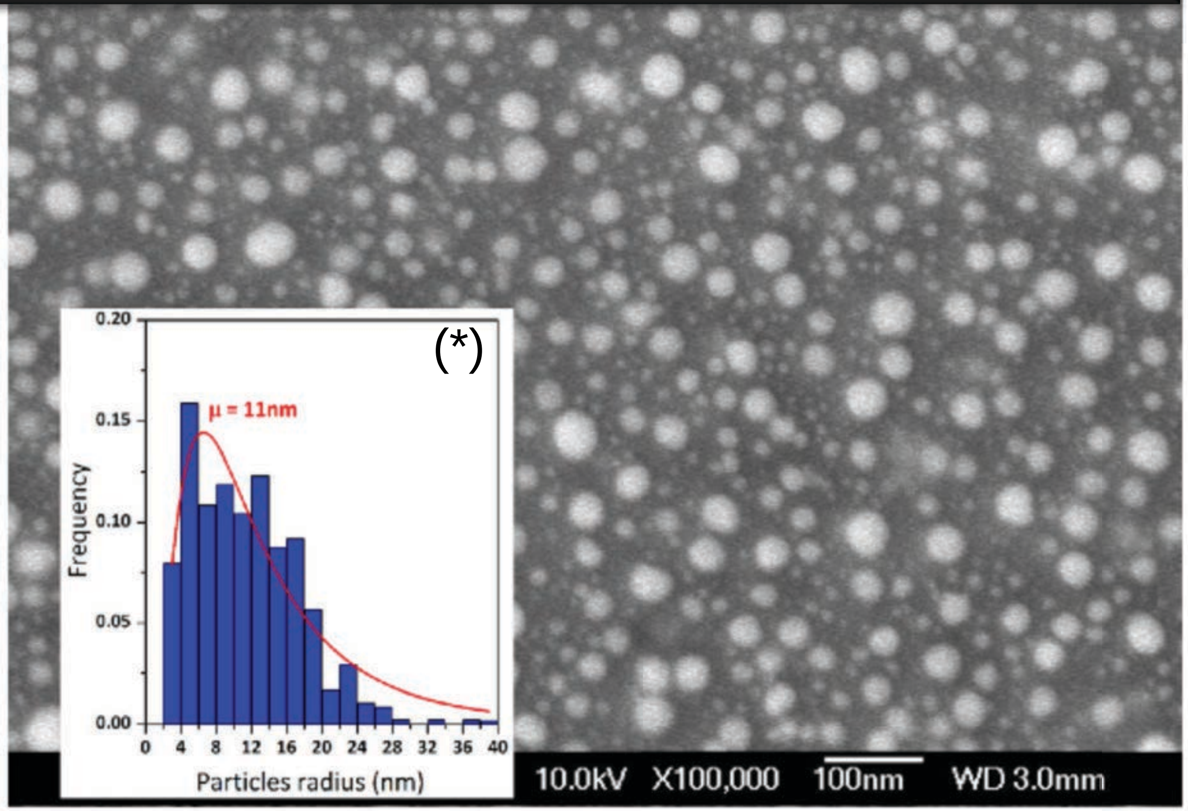
$$\tau = \int_0^t 16\pi R_1^2 . \left(\frac{kT(t')}{\pi m_1}\right)^{\frac{1}{2}} . \frac{N}{V(t')} dt'$$

NP size ditribution fct of a single parameter: condensation rate τ

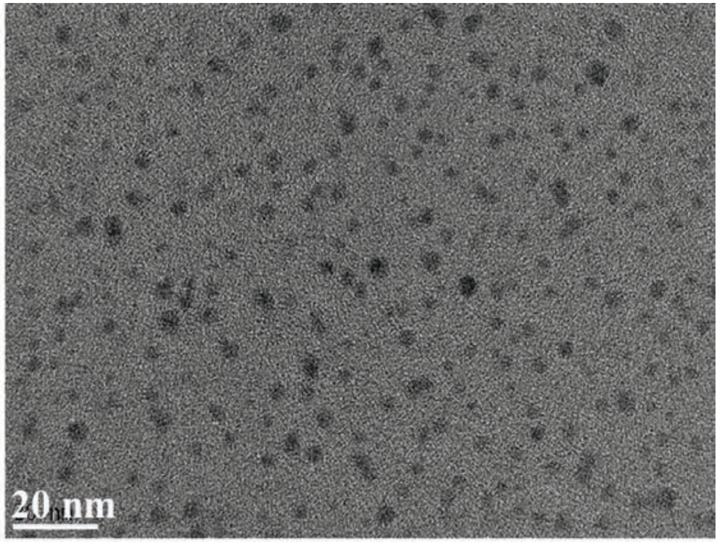


Soler, Phys. Rev. Lett. 49, (1982)

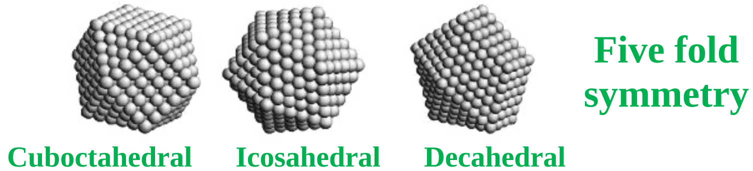
NP examples - Nanostructures

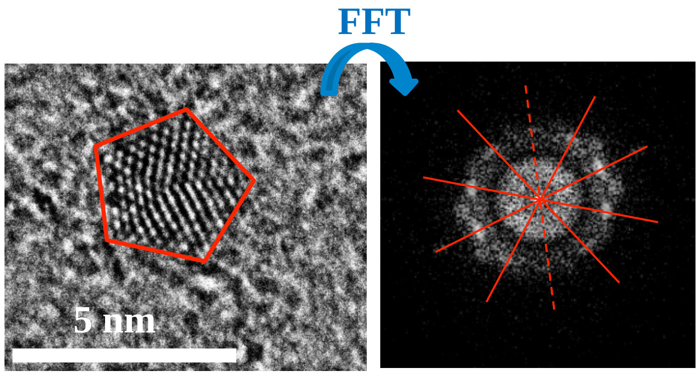


Silver nanoparticles



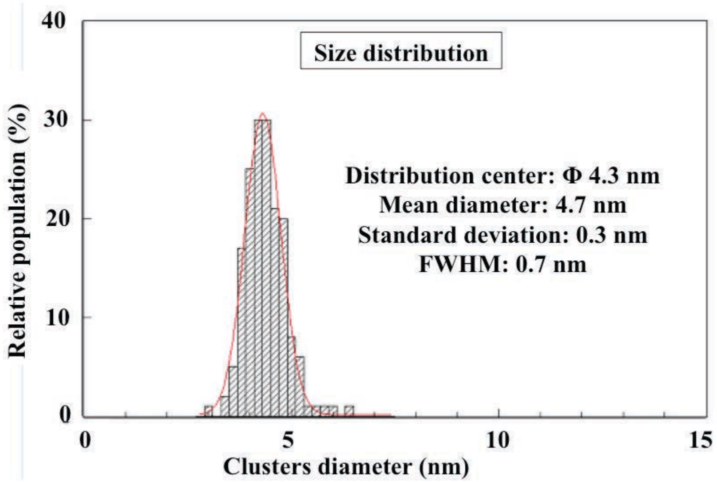
HR-TEM image of Silver NPs embedded in amorphous C-matrix



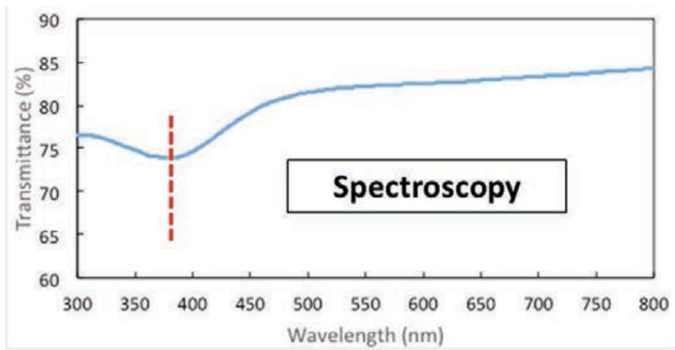


Isolated Ag NP

↳ NPs well **crystallised** in **fcc** structure **at RT**



↳ **Narrow** size distribution



Surface Plasmon Resonance of silver at λ = 379 nm

↳ NPs keep their **metallic nature**

NP growth: homogeneous nucleation theory

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Kinetic equations for NP-NP reactions:

$$\frac{dn_k^*}{d\tau(t)} = \sum_{\substack{i+j=k \\ i\leq j}} C_{ij}^* . n_i^* . n_j^* - \sum_i C_{ik}^* . n_i^* . n_k^*$$

First term: Formation rate of k-sized NP resulting from the coalescence of a i-NP and a j-NP

Second term: Number of events where k-sized NPs form bigger NPs

C_{ij}: coalescence probability between a i-NP and a j-NP

$n_i^* = \frac{N_i}{N}$ reduced variable

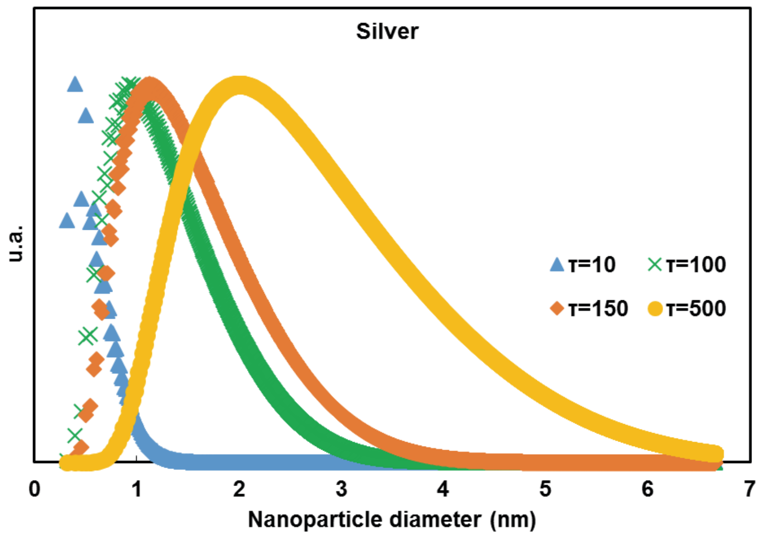
n^*_i: number of i-sized NPs

n^*j: number of j-sized NPs

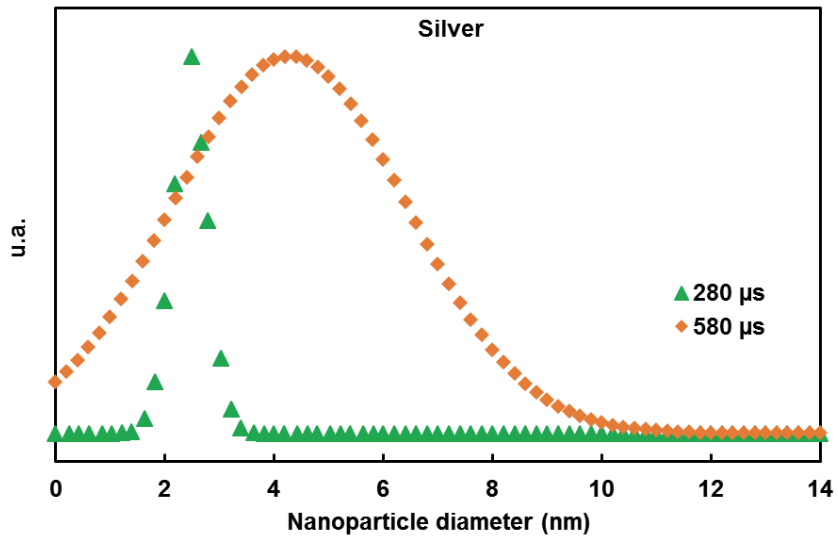
NP size ditribution fct of a single parameter: condensation rate τ

$$\tau = \int_0^t 16\pi R_1^2 . \left(\frac{kT(t')}{\pi m_1}\right)^{\frac{1}{2}} . \frac{N}{V(t')} dt'$$

Theoretical



Experimental (data collected from TEM images)



Soler, Phys. Rev. Lett. 49, (1982)

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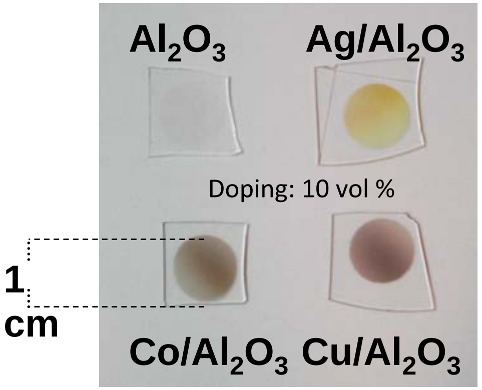
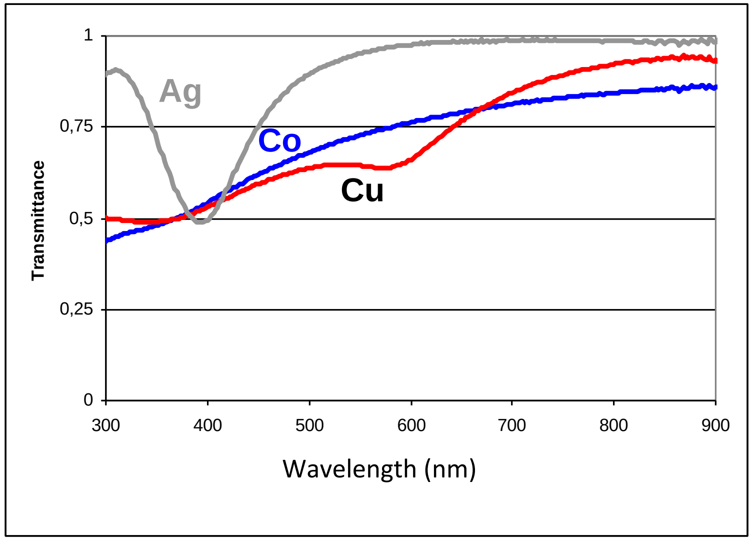
Ag, Co, Cu- NPs in PLD-Al2O3 matrix

Optical properties

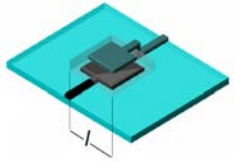




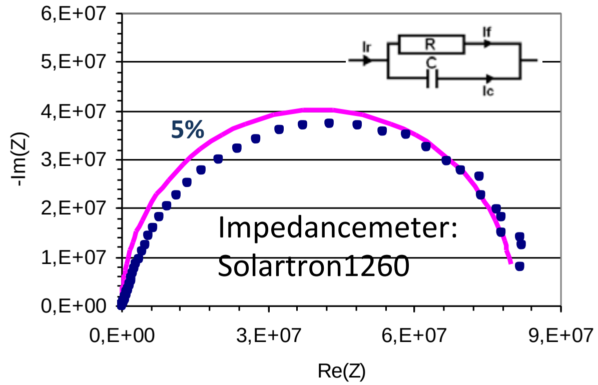
Electrical properties*

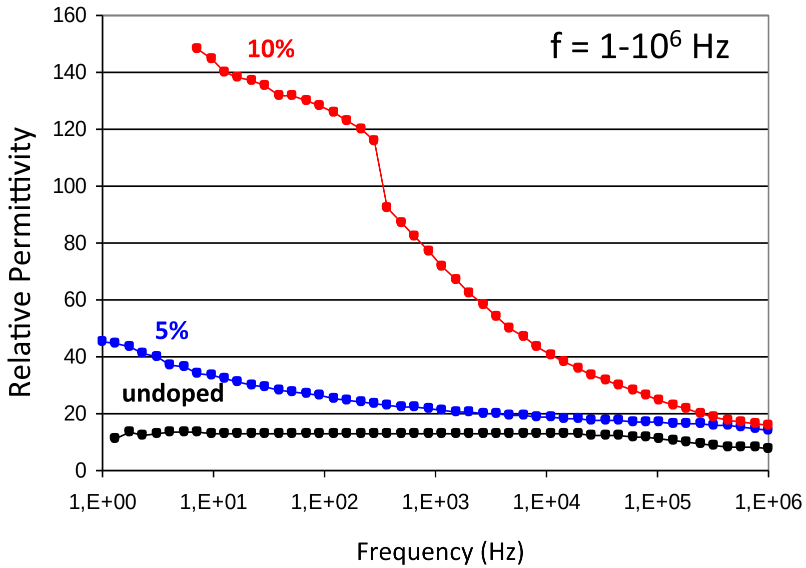
$$Zt = \frac{R}{1+R^2.C^2.\omega^2} - j\frac{R^2.C.\omega}{1+R^2.C^2.\omega^2}$$

MIM structure



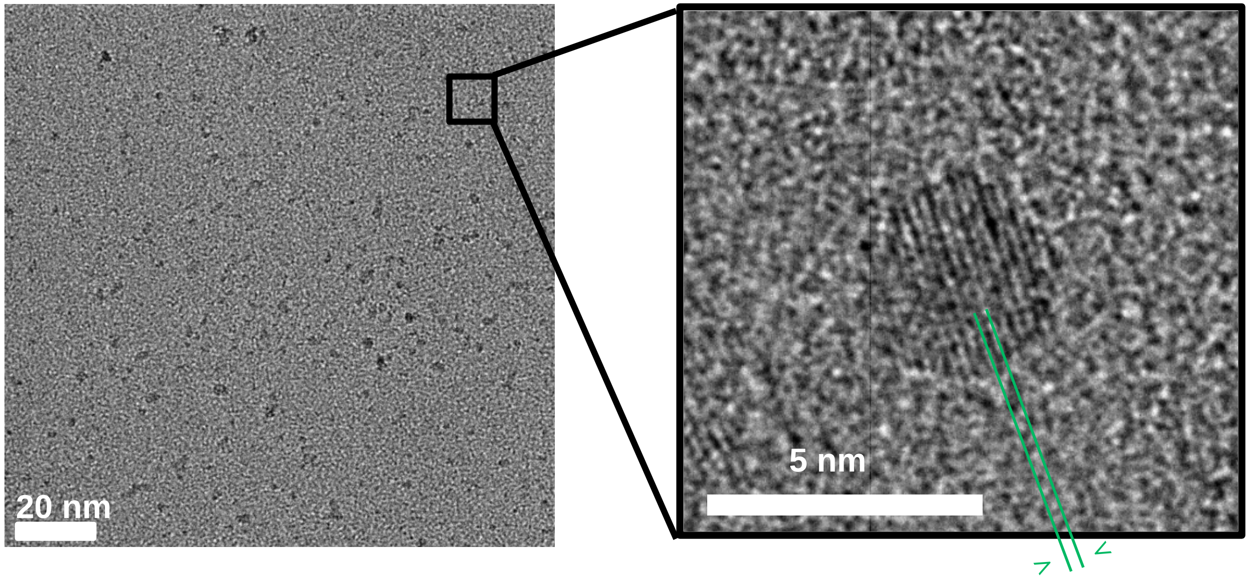
$$C = \varepsilon_r.\varepsilon_0.\frac{S}{d}$$



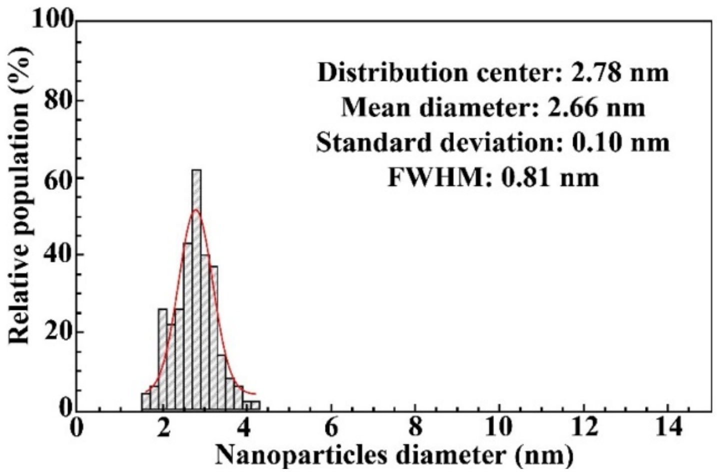


*Crunteanu, Dumas-Bouchiat, Champeaux, Catherinot, Blondy, Thin Sol. Films 16 (2007)

Vanadium NPs



HRTEM image of Vanadium NPs embedded in amorphous Al_2O_3 matrix



➥ NPs well **crystallised** in **cc** structure **at RT**

- **Crystallised ~3 nm metallic NPs at RT, sharp size distribution**
- **High deposition rate (50 nm of V-NPs per 15 min)**
- **Flexible choice of materials:**
  - **Isolated NPs embedded in different matrix**
  - **Stacks of NPs (porosity properties)**

Vanadium dioxide (VO2) thermochromic mat.

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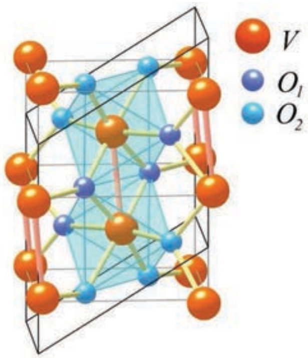
Reversible first order Insulator to Metal Transition at ~68°C (close to RT)

VO_2 properties

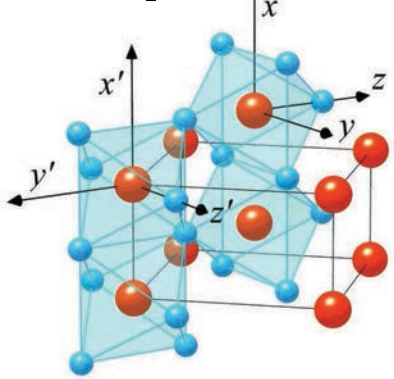
- **Semi conductor at Low Temperature**
- **Metallic at High Temperature (T > 68°C)**

T ↗

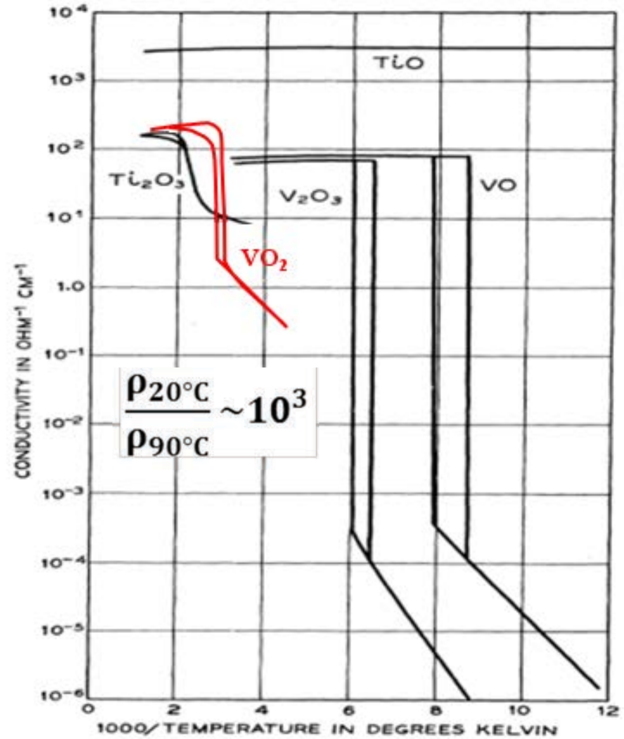
Monoclinic phase



Rutile phase



Extracted from ref [1]



➯ Abrupt changes in electrical resistivity and optical properties (IR range)

[1]J.F. Morin, Physical Review Letters, 1959

Nanosized VO_2 NPs vs VO_2 PLD thin films

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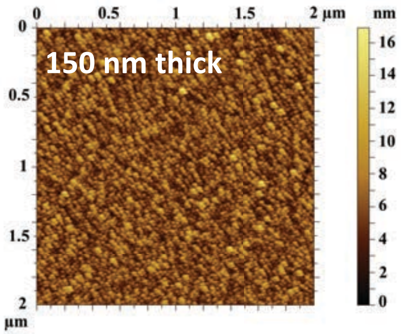
V NPs

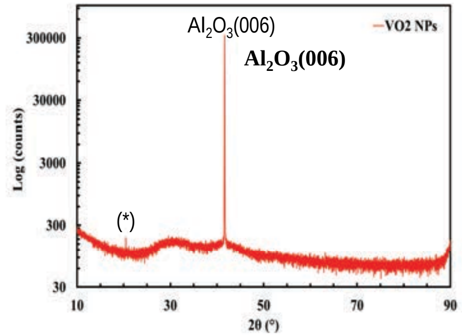
post annealing @ 300°C, P_{O2}: $3.3.10^{-2}$ mbar, Al2O3, MgO or Glass substrate

VO_2 NPs

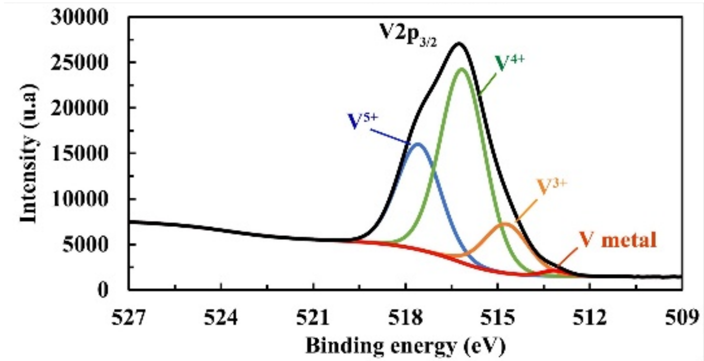
AFM



XRD



X-ray photoelectron spectrometry XPS



Only substrate peaks

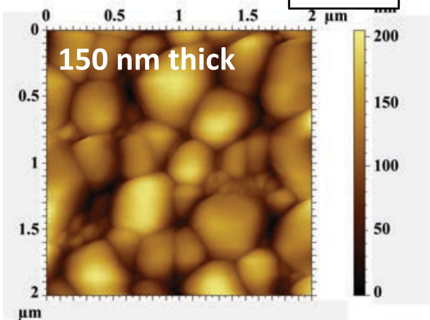
No peak of VO_2; no long range order

VO_2 major phase

PLD VO_2 thin film

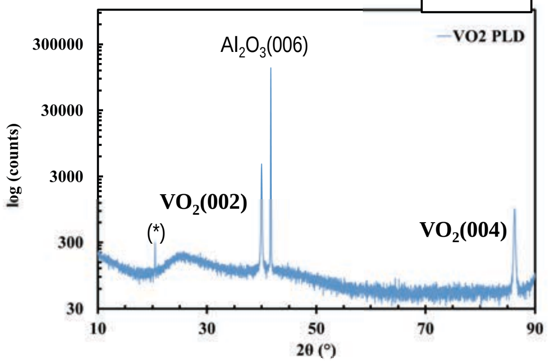
deposited at 700°C, P_{O2}: $2.2.10^{-2}$ mbar, Al_2O_3 substrate

AFM



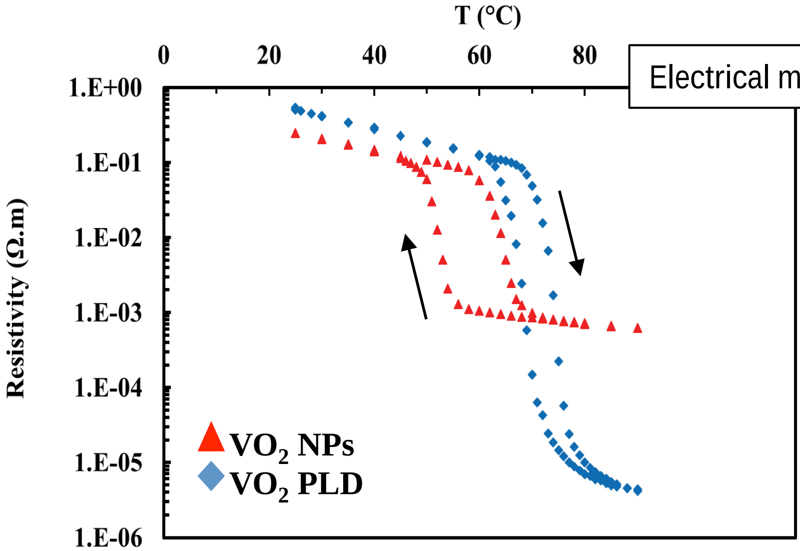
↳ ~150-200 nm sized grains

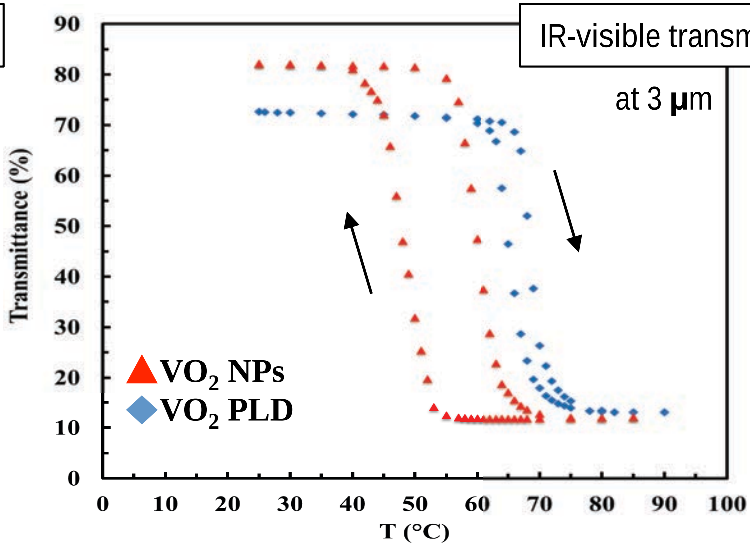
XRD



- well cristallized mono-oriented (020) VO_2 film

Nanosized VO_2 NPs vs VO_2 PLD thin films[1]





Measurement	Tc(°C)	ΔT(°C)	ΔA
VO2 NPs			
Transmittance	54	12	8
Resistivity	58	12	4.10^2
VO2 PLD			
Transmittance	68	3	5.5
Resistivity	72	5	1.10^5

NPs vs dense films

- Increase of hysteresis width
- Decrease of T_{MIT}

[1]ANR Project MUFRED 2017-2019: VO_2 integration in microsystems:
SPCTS, Xlim Limoges, LMGP Grenoble, IETR Rennes, Thales Paris, Lab-STICC Brest

***Gaudin, Champeaux, Dumas-Bouchiat «From metallic vanadium nanoparticle assemblies to thermochromic VO2 behaviour»*, submitted**

Combine VO_2 NPs & VO_2 PLD thin films

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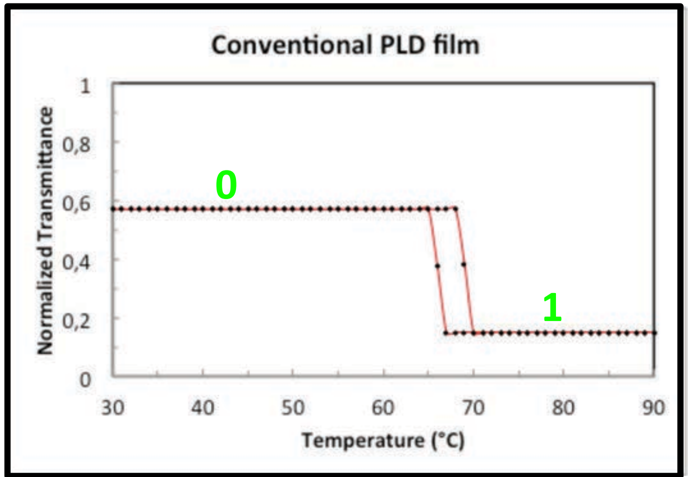
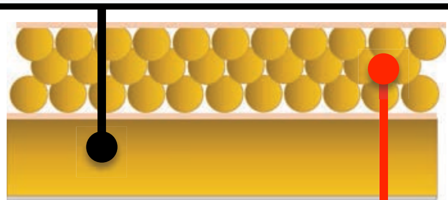
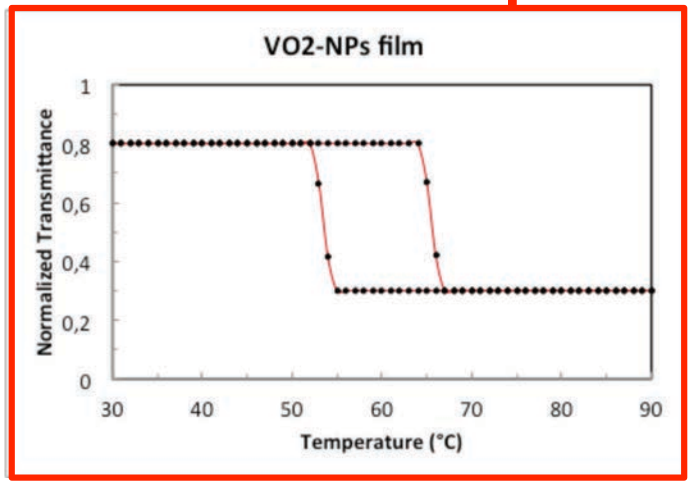
T_{max}=0.57, T_{min}=0,15, $T_{transition}$=68°C, hysteresis width: 2°C



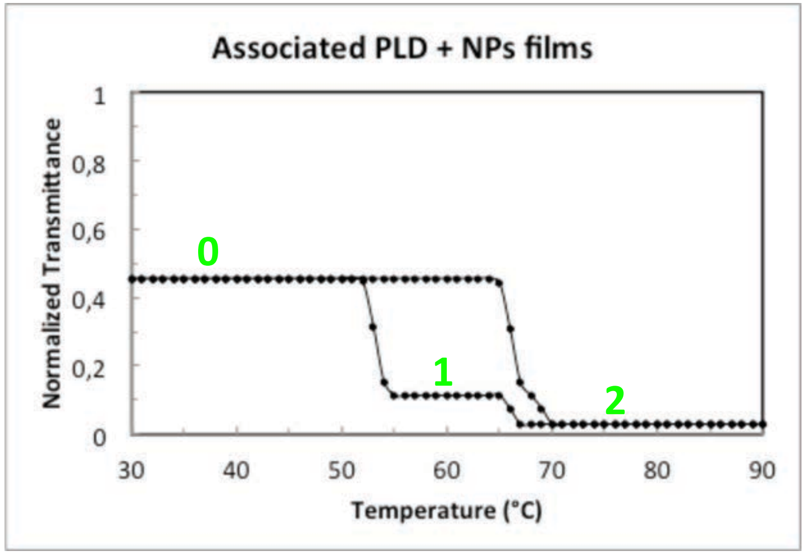
100 nm

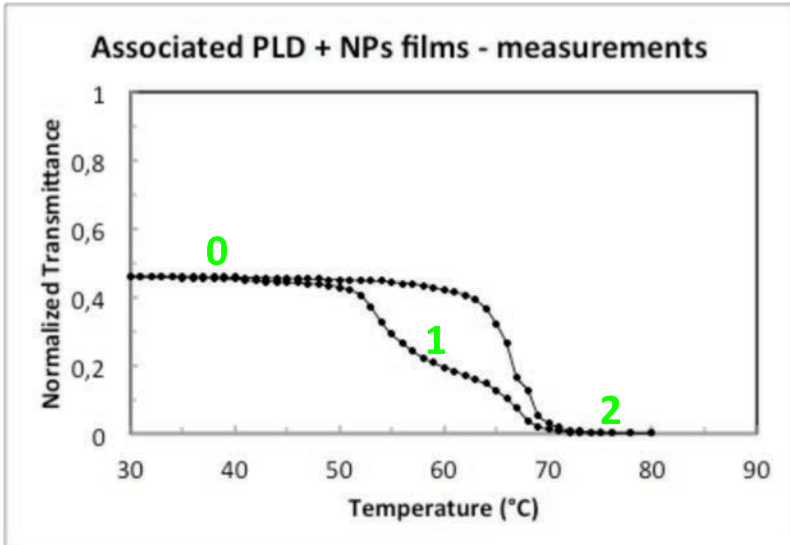
100 nm



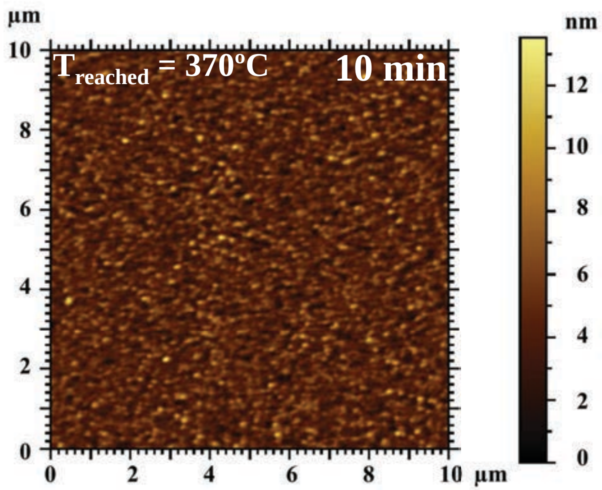


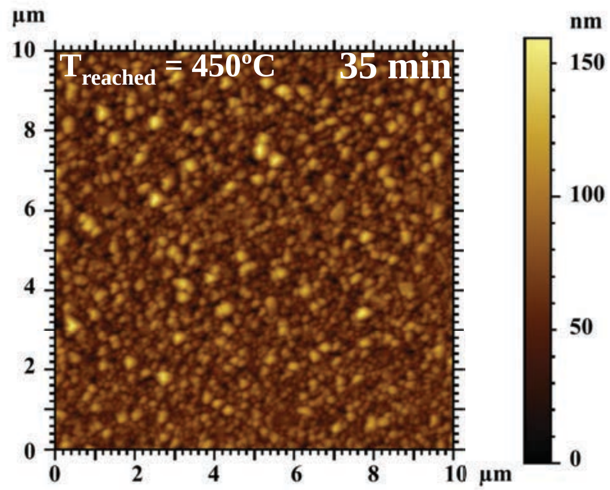
T_{max}=0.80, T_{min}=0,20, $T_{transition}$=60°C, hysteresis width: 10°C

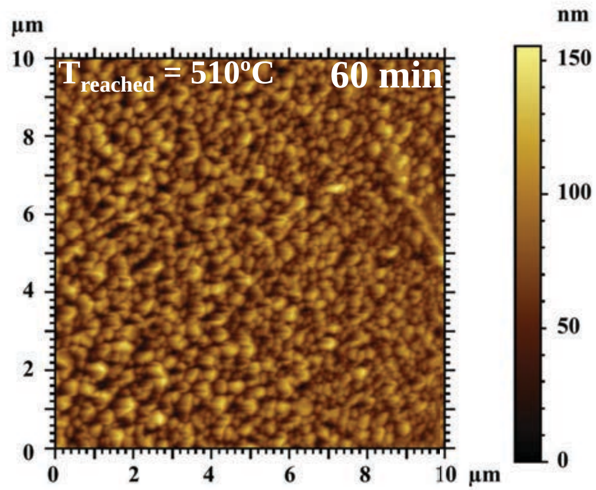




Nanocomposite: VO_2 NPs/Thin films

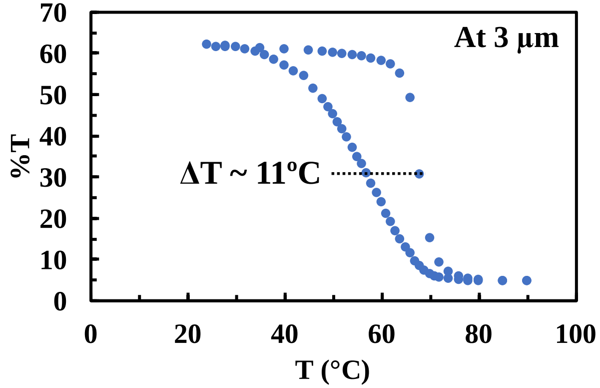


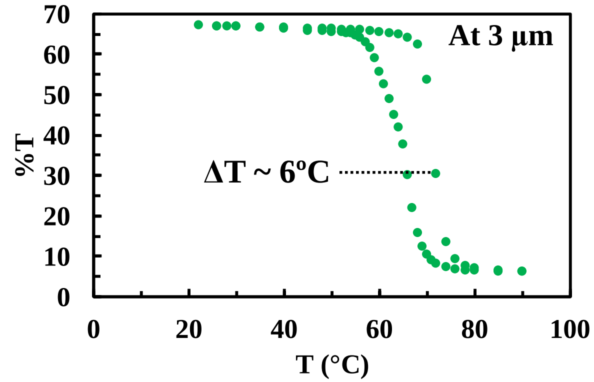


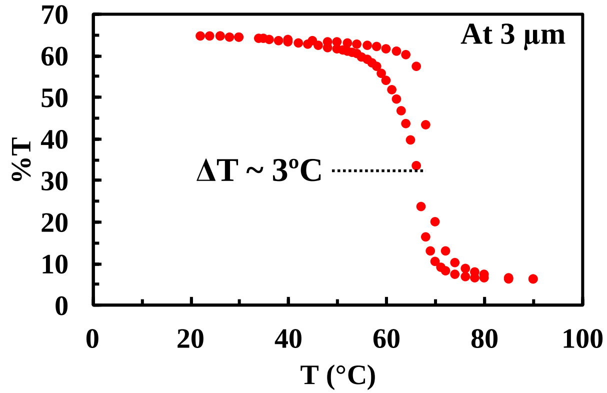


NP size		
< 10 nm	60-80 nm	120-150 nm

↳ **Coalescence and NPs growth** observed with annealing time

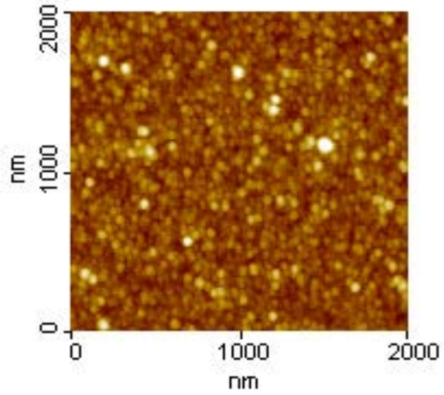




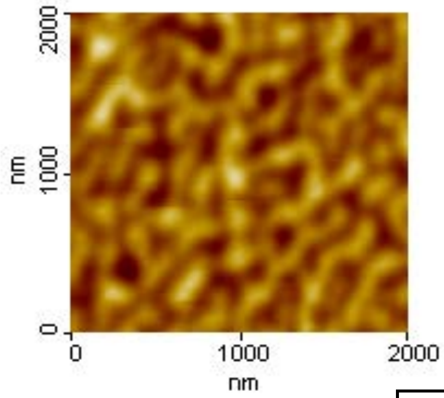


Cobalt NPs: stacking

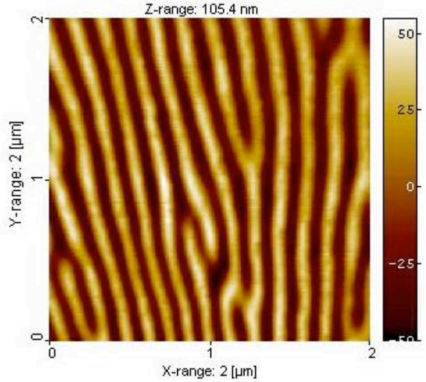
a) topographic signal



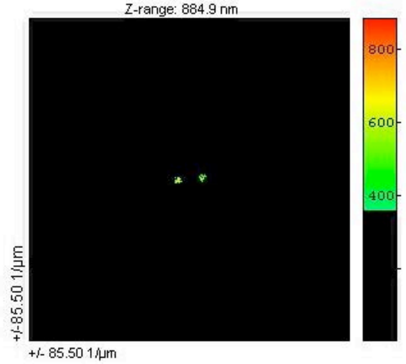
b) MFM signal

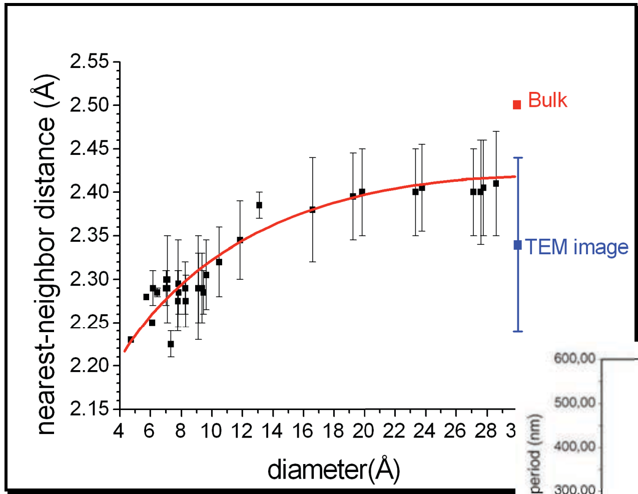


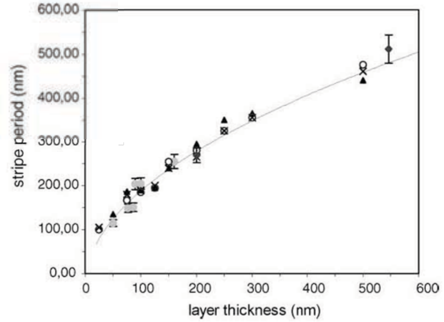
c) MFM signal



d) FFT





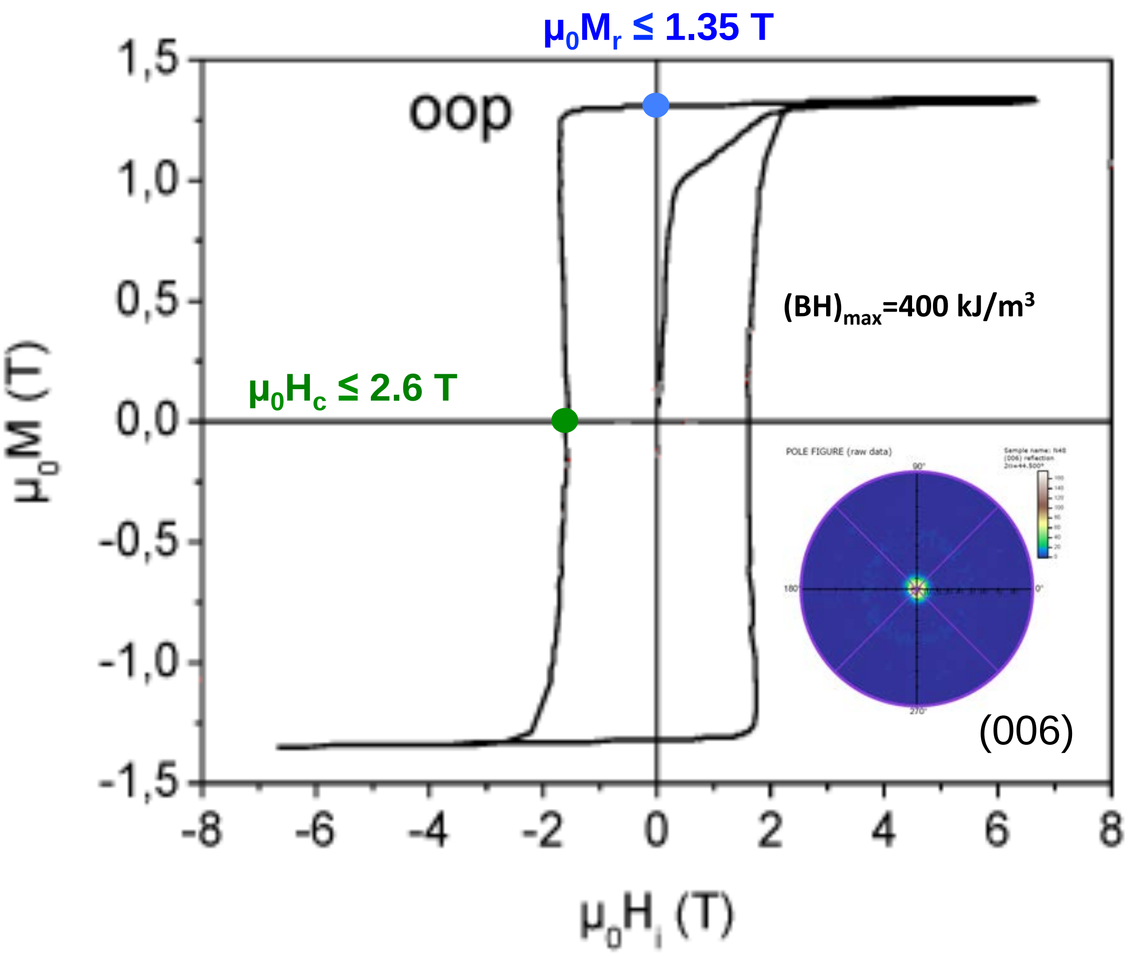


- Contraction of the crystal lattice[1]
- Exhibition of a √t dependance[2]
- Chudnovsky model: magnetic entity 9nm[3]

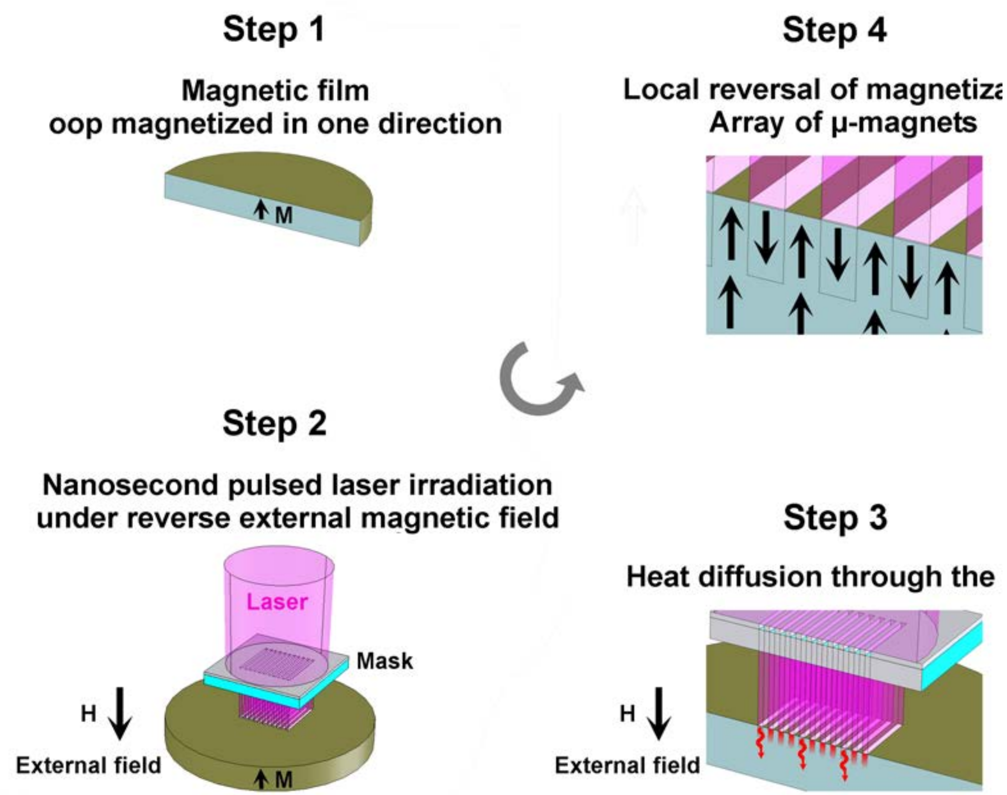
[1]*Rives, Phys. Rev. B 77 (2008)*
[2]*Dumas-Bouchiat, Appl. Surf. Sci. 247 (2005)*
[3]*Dumas-Bouchiat, J. Appl. Phys. 100 (2006)*

Applications, playing with magnetic NPs …

Hard magnetic film
Grenoble/institut Neel/ N.M. Dempsey

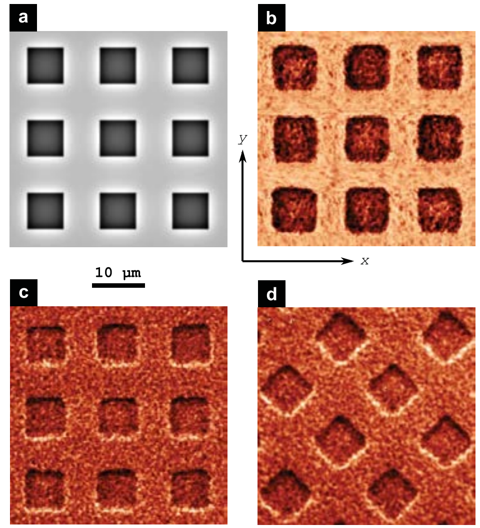


Focus on Thermo-Magnetic Patterning: TMP



- Laser fluence adapted not to damage the film
- Magnetisation reversed on 1.5 μm

IEEE Front Cover, sept 2016



IEEE TRANSACTIONS ON
MAGNETICS

A PUBLICATION OF THE IEEE MAGNETICS SOCIETY

SEPTEMBER 2016 VOLUME 52 NUMBER 9 IEMGAQ (ISSN 0018-9464)

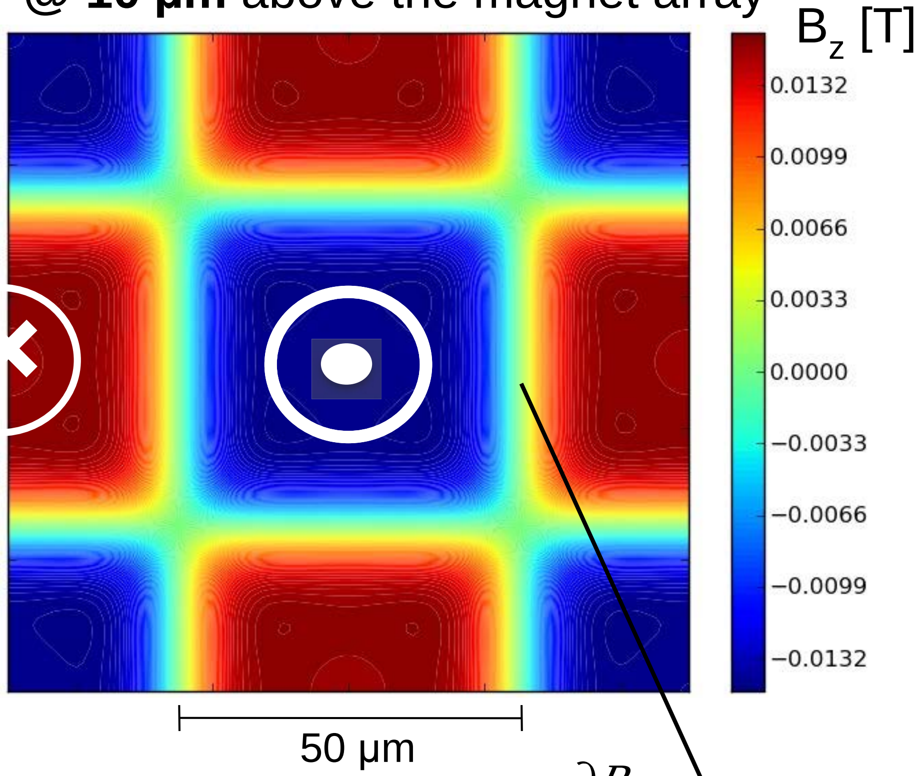
(a) Calculated map of the vertical component of the stray field at a height of 100 nm above the patterned SmCo film. (b) Phase shift map measured with a flexible cantilever soft coating probe. (c) and (d) Phase shift maps measured with a stiff cantilever hard coating probe. From the paper, "Some Aspects of Magnetic Force Microscopy of Hard Magnetic Films," by G. Ciuta *et al.*, Art. no. 6500408.

IEEE

Magnetic stray fields & forces

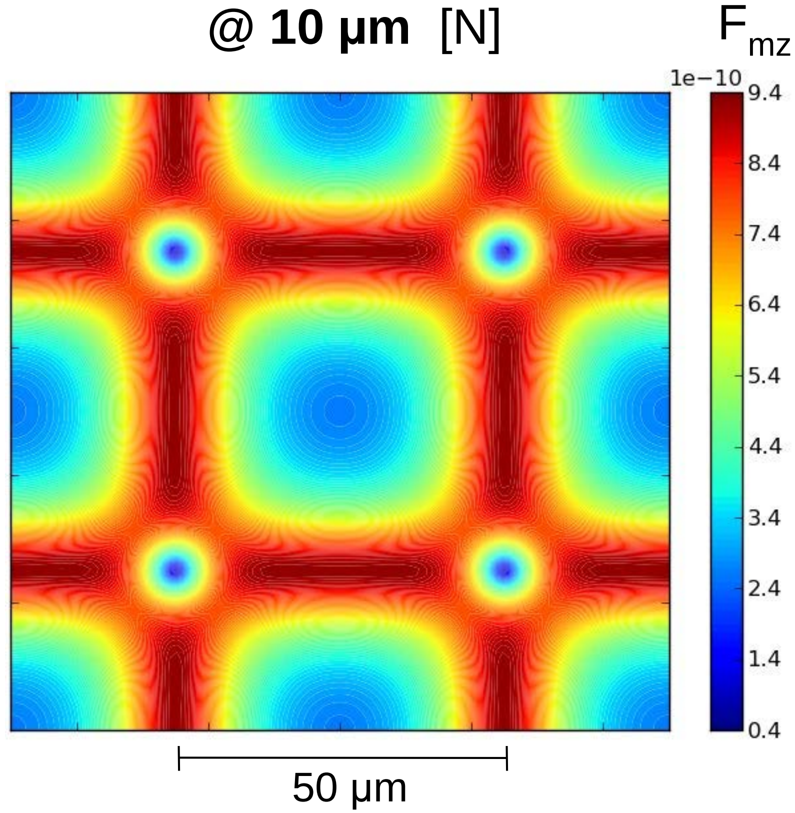
Superparamagnetic NPs ø 3 µm
20 % wt Fe_3O_4 80 % wt Polystyrene

Z-component of the magnetic stray field
@ **10 µm** above the magnet array



$$\frac{\partial B}{\partial z} = 10^6\,\mathrm{T/m}\ @\ 2\ \mathrm{nm}$$

Z-component of the attraction force
@ **10 µm** [N]



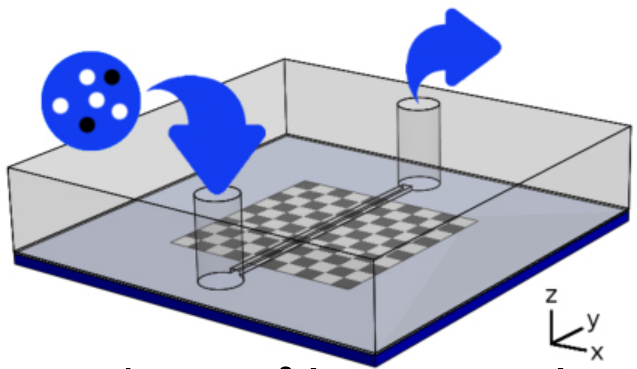
@ 10 µm above

- Magnetic field → tens of mT
- Magnetic trapping force → hundreds of pN

Microfluidic potential: NPs sorting

µ-fluidic channel in PDMS, width = 500 µm, t_{PDMS} on film ≈ 10 µm

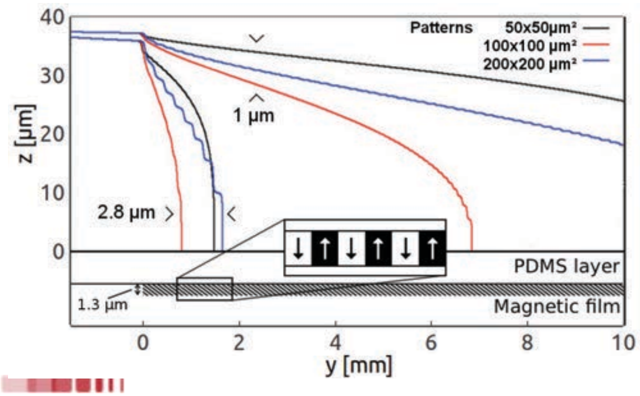
NPs sorting by trapping



$F_g = 4/3\ \pi\ r_{bead}^3\ (\rho_{bead} - \rho_{medium})\ g$

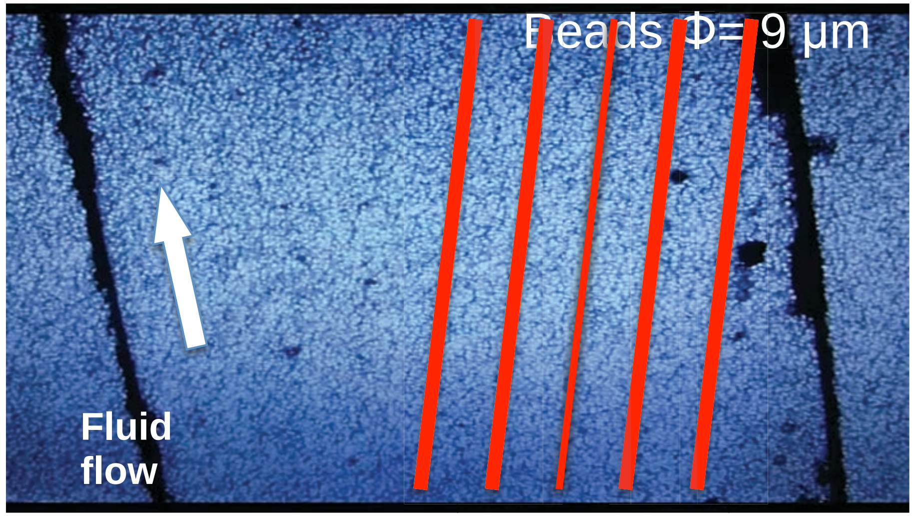
$F_d = 6\ \pi\ \eta\ r_{bead}\ (\upsilon_{fluid} - \upsilon_{bead})$

$F_m = \mu_0\ V_{mag}\ M\ \nabla H$

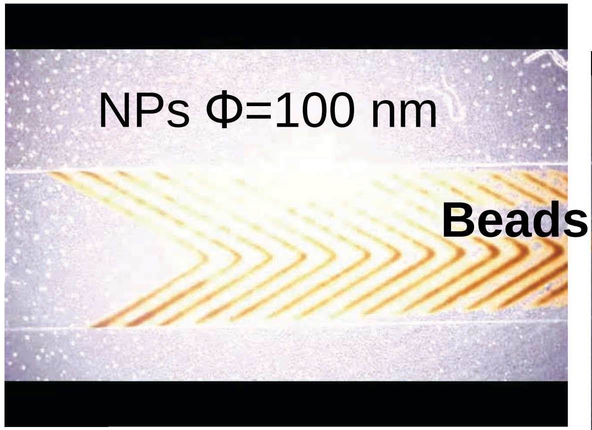


- No external magnetic field
- No power source
- Stray fields restric. to the region of interest
- Adapted to space restricted (microscopy)

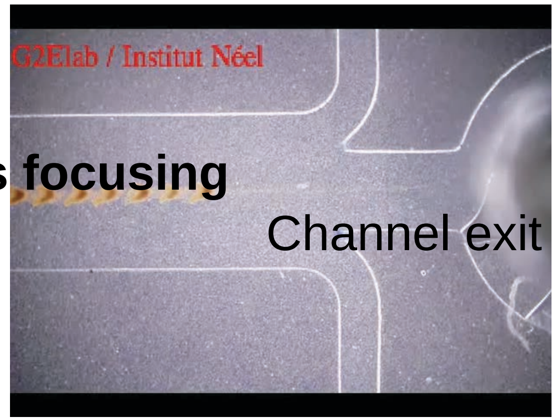
NPs sorting by guiding: Dynamic mode



Channel entrance

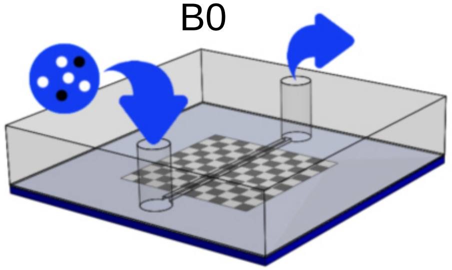


Beads focusing

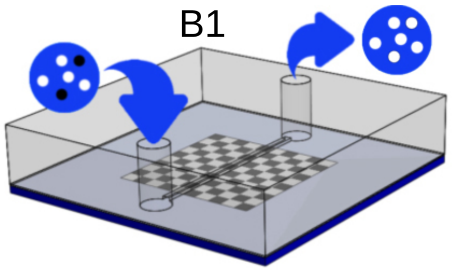


High gradient magnetic separation-HGMS

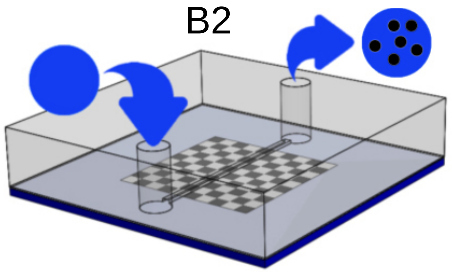
B0: initial composition
65.6% PS NPs
34.4% Magnetic NPs



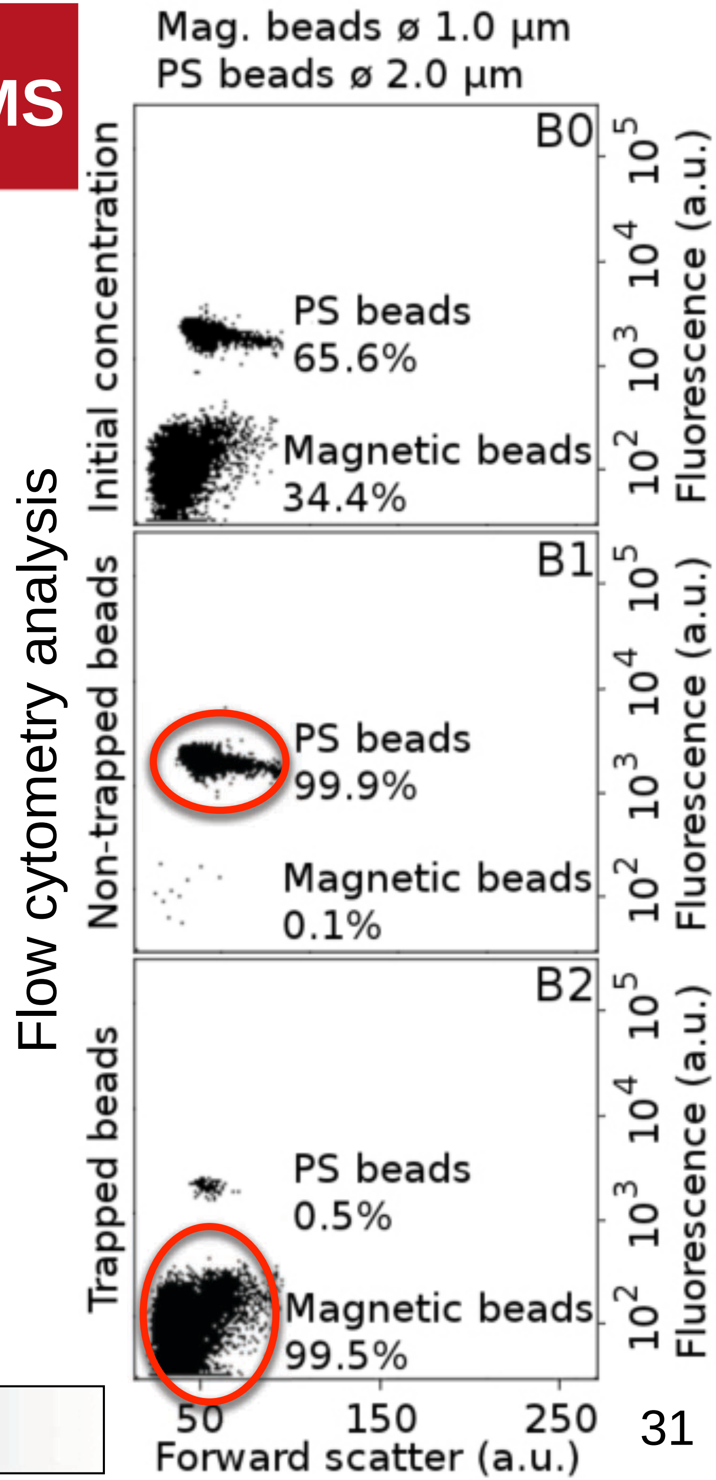
After a first pass throught the channel
B1: selected solution
99.9% PS NPs



high fluid flow to clean the channel
B2: solution with magnetic beads
99.5% Magnetic NPs



- Highly efficient for NPs
- Highly efficient for tag Cells (Jurkat & HEK) 95% / 5%



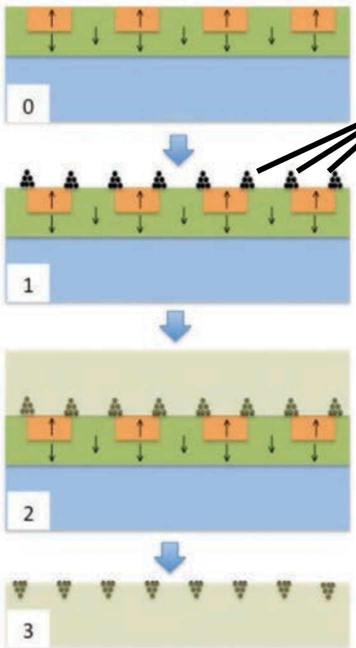
HGMS → Zanini Appl. Phys. Lett. 99 (2011)
Bact. Magn. Sorting → Pivetal Sens. & Act. B 195 (2014)

μ-magnetic imprinting MMI, N.M. Dempsey

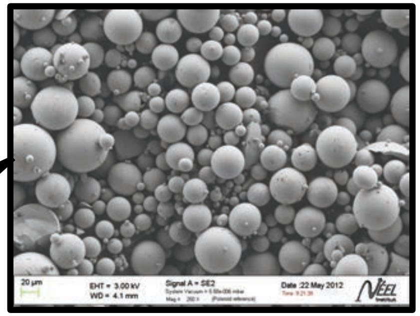
0 - TMP structure
1 - Hard magnetic beads sprinkled onto master structure and concentrated at the interfaces of micro-magnets
2 - polymer binder poured over the hard magnetic beads
3 - Solid composite peeled off the master structure

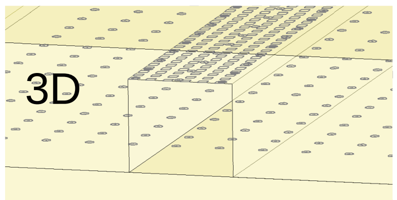
Magnequench® NdFeB powders GA50

MMI

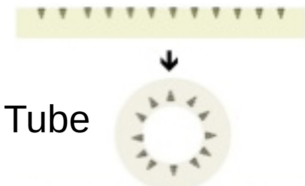


and magnetized





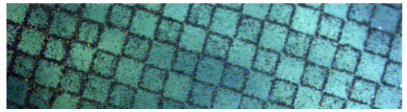
Tube



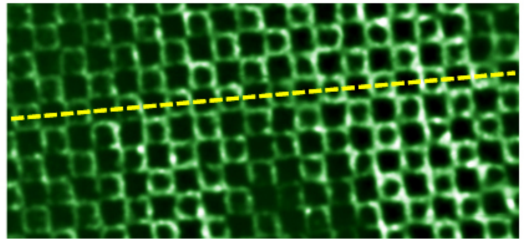
- Cheap
- Flexible
- Transparent
- Biologicaly compatible
- One Master for thousands prototypes

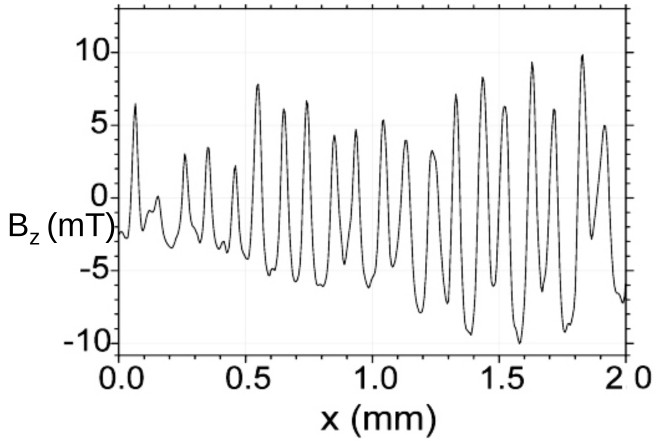
Example of magn. polymer structures

Optical image



Scanning μ-Hall probe





Extract the B_z magnitude

Dempsey, Dumas-Bouchiat, Givord, Zanini Patent FR1254667 (2012), US 61/650,398 (2015)
Soft magn- materials → Leroy Mat. Today Comm. 1 (2016)

Other Free NP sources

Vanessa Orozco Montes, Cedric Jaoul, Pascal Tristant

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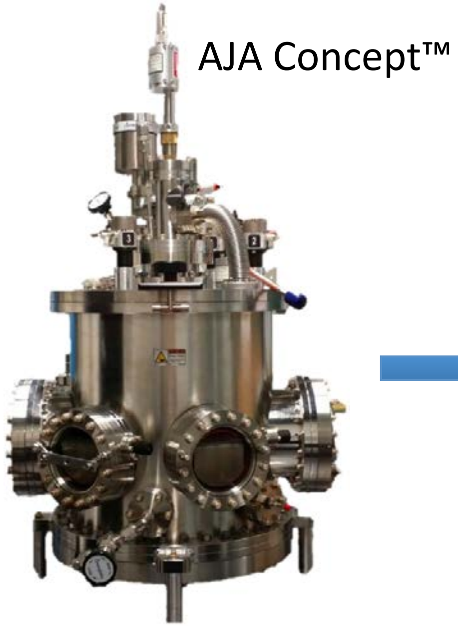
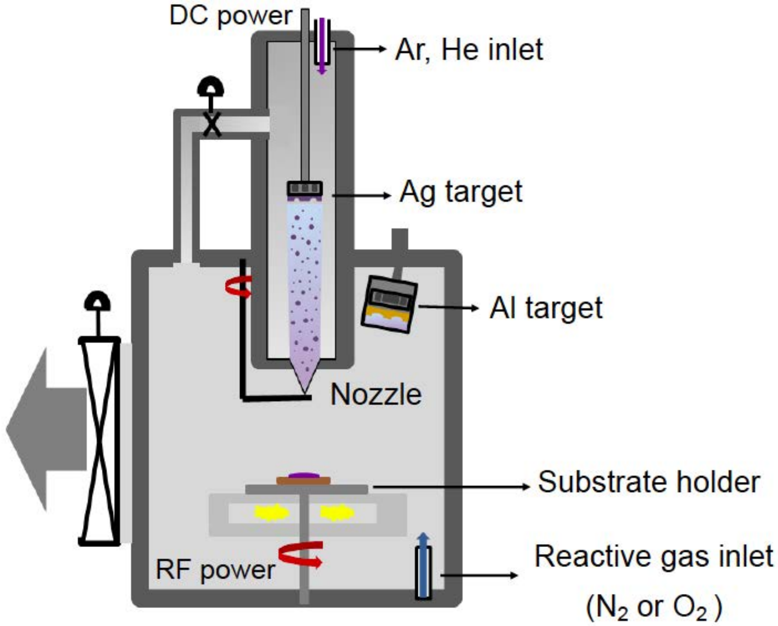
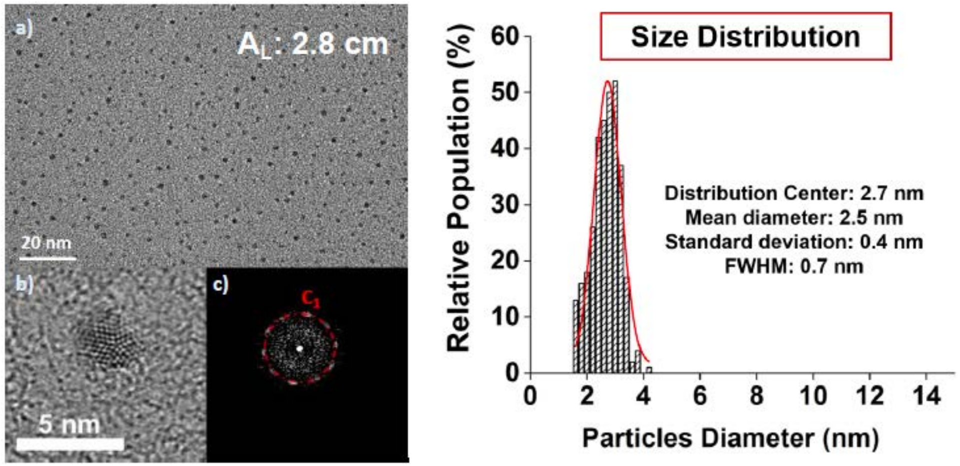
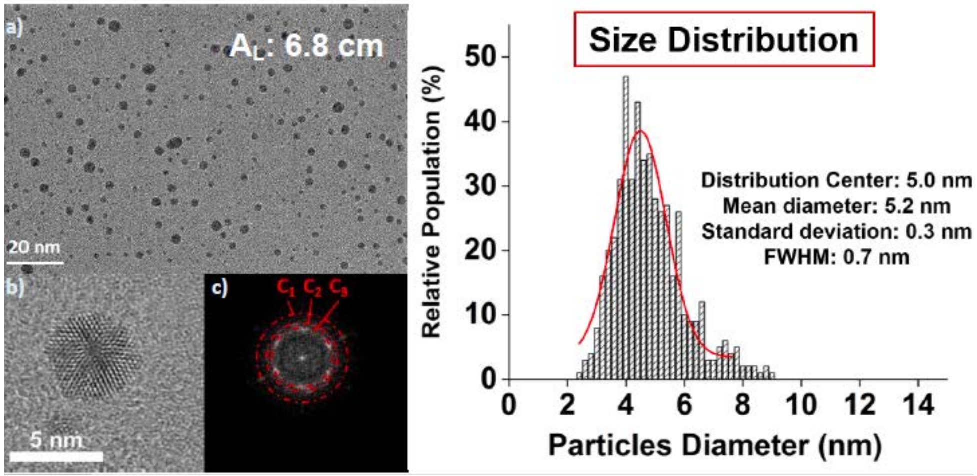
Limoges Free NP source based on magnetron sputtering

Poster:
Optical Emission Spectroscopy









Orozco Montes, Free Ag & Cu NPs based on magnetron sputtering, Best Poster Award E-MRS (2016)
Orozco Montes, Electrical behavior of Al2O3 films doped with Ag NPs, Best Poster Award Electroceramics XV (2016)

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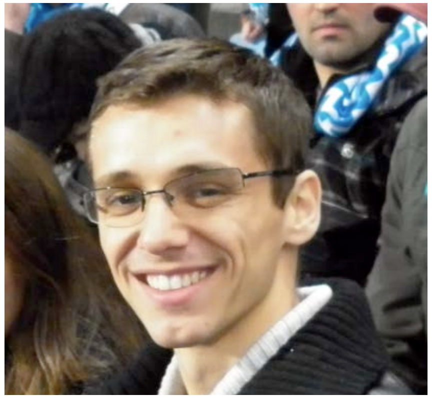
Many thanks to students and especially:

2009-2012



Luiz Fernando Zanini

NÉEL institut

Agence Nationale de la Recherche ANR

2013-2016

Michael Gaudin

LABEX Σ LIM

2014- …

Maileth Vanessa Orozco Montes

Région LIMOUSIN

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Science des Procédés Céramiques et de Traitements de Surface

Thank you for your attention