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Sputtering onto liquid substrates, Towards the synthesis of nanoparticles

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David Cornil, Jérôme Cornil, and Stephanos Konstantinidis

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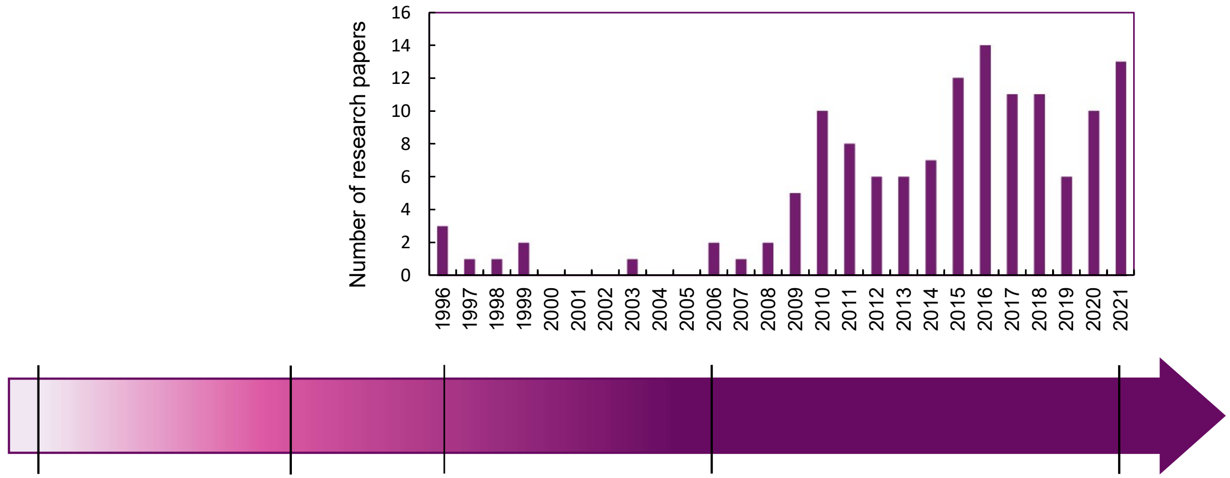
Sputtering onto Liquids (SoL)



1852
Sputtering onto solid substrate

1974
Evaporation onto silicone oil

VEROS process
Nagoya University

1996
Sputtering onto silicone oil

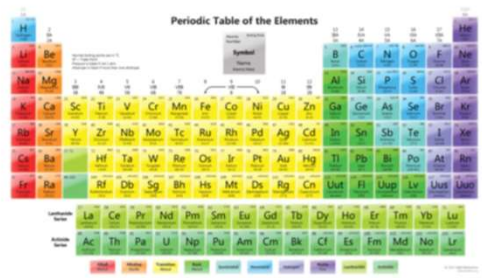
2006
Sputtering onto ionic liquids

Nagoya University

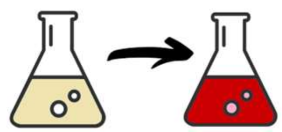
December 2021
More than 135 research papers were published since 1996

A. Sergievskaya, A. Chauvin, and S. Konstantinidis, *Beilstein J. Nanotechnol.* **13**, 10 (2022)

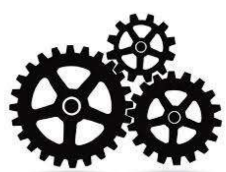
What are the advantages of SoL technique ?



Flexibility



Purity



Safety & Reproducibility

Our goal

PLASMA WORKING PARAMETERS

- Nature of sputtered material
- Nature of the liquid
- Sputter power
- Target – substrate distance
- Pressure
- Kind of sputtering process, ...

PLASMA PROPERTIES

- Particle fluxes
- Kinetic energies

PLASMA LIQUID INTERACTIONS

- **Heating of the host liquid by plasma**
- Chemical modification of the host liquids…

NANOPARTICLE FORMATION

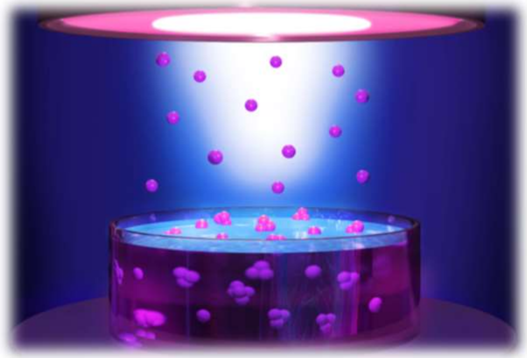
- **How do the NP grow?**
- Can we control the size, shape, elemental composition of NPs?
- Are NP solutions stable?

PRODUCT PROPERTIES

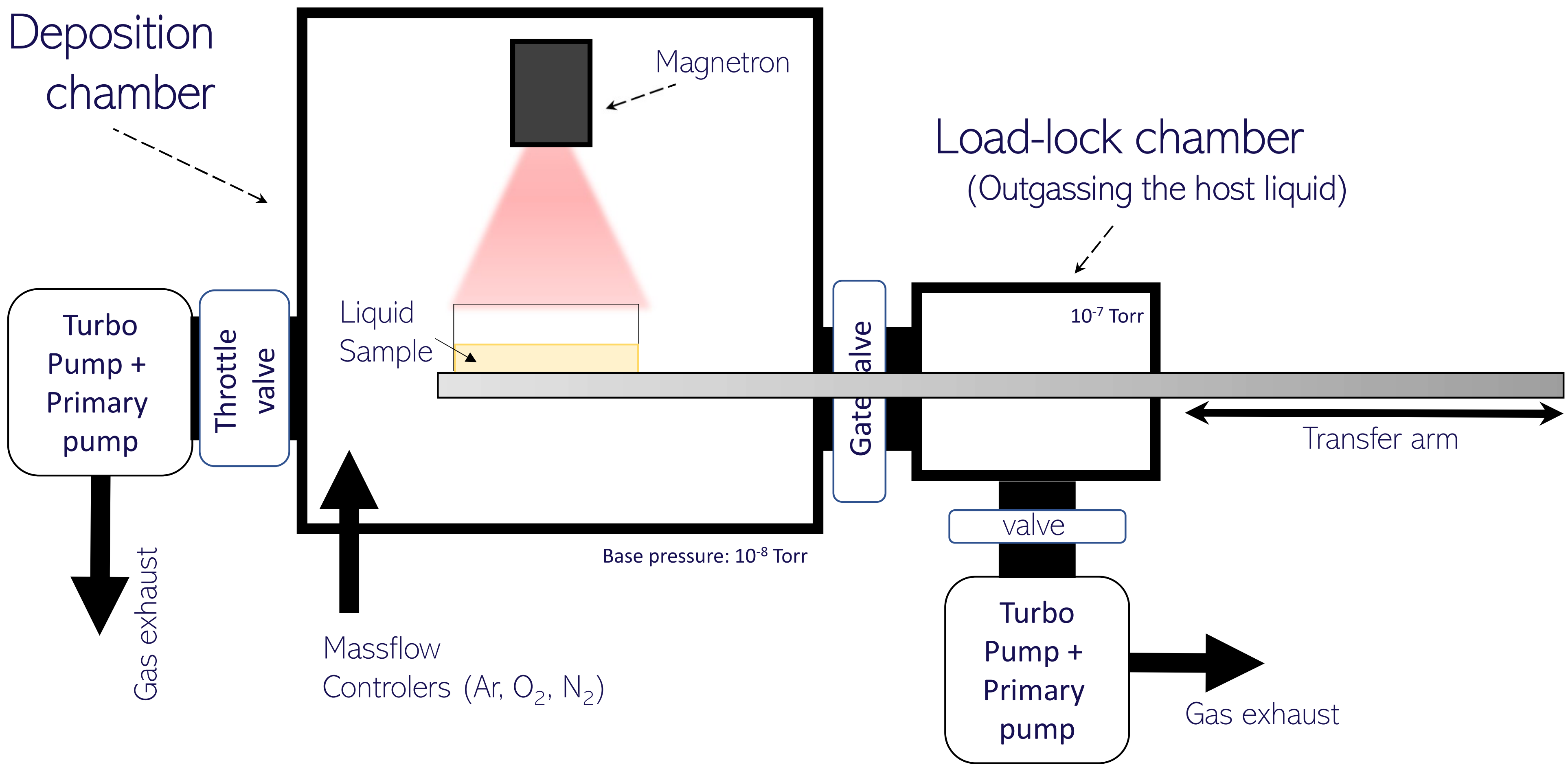
- Characterization of colloidal solutions and individual NPs

APPLICATIONS

- Collaboration with other research groups



Experimental set-up



Playing with the working conditions

Varying parameters are:

Plasma

1. Deposition time
2. Sputter power
3. Working gas pressure
4. Kind of sputtering discharge (DCMS vs. HiPIMS – unipolar and bipolar)
5. Sputtered metal (Au, Ag, Cu)

Liquid host

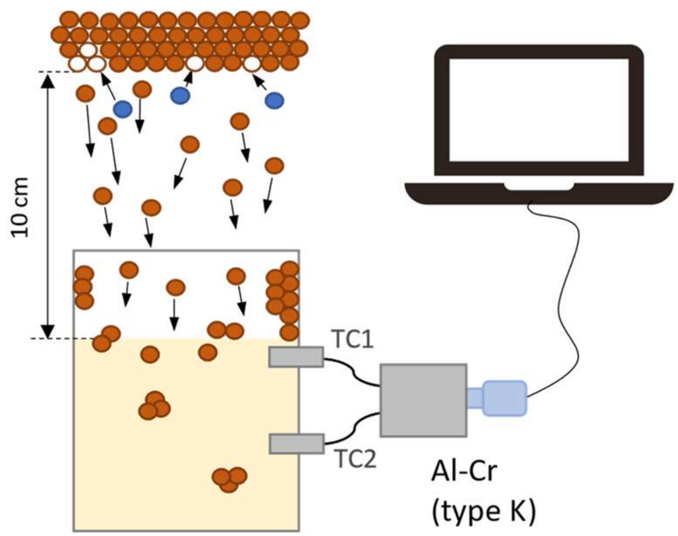
6. Host liquids (vegetable oils, silicone oil, PEGs)
7. Viscosity of the host liquid
8. Stirring of the solution during the deposition

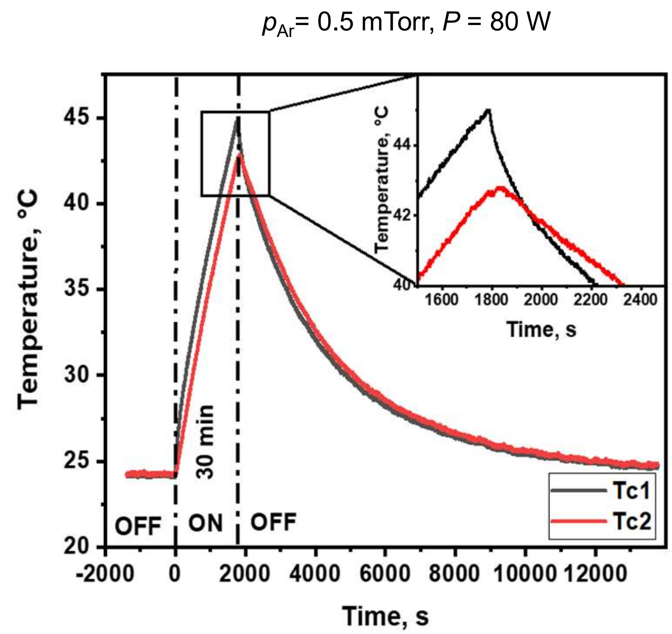
Main methods of NP characterization:

1. Ex situ and operando UV-Vis spectroscopy: optical properties, colloidal stability and ageing of NP solutions
2. TEM: size and size distribution of NPs

Plasma-liquid interactions: heating of the liquid substrate

2-inch copper target, WD = 10 cm, 4 g of castor oil, 30 min of sputter time

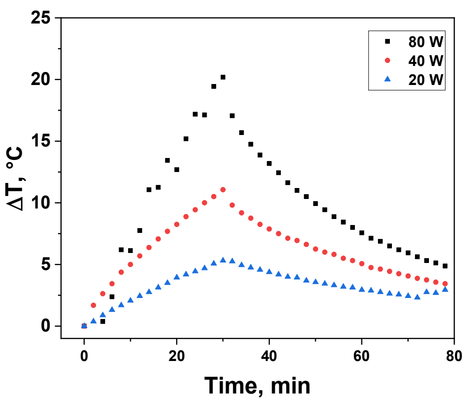


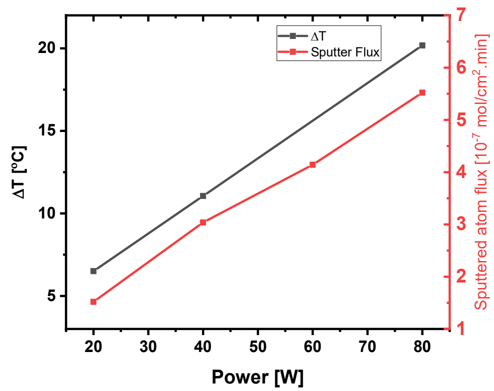


K. Patel, A. Sergievskaya, S. Chauhan, S. Konstantinidis, *J. Appl. Phys.* **131**:203301 (2022).

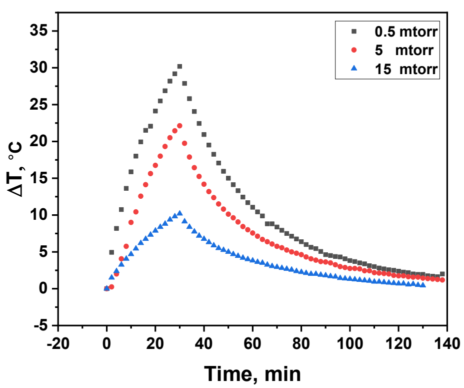
The plasma heats the liquid

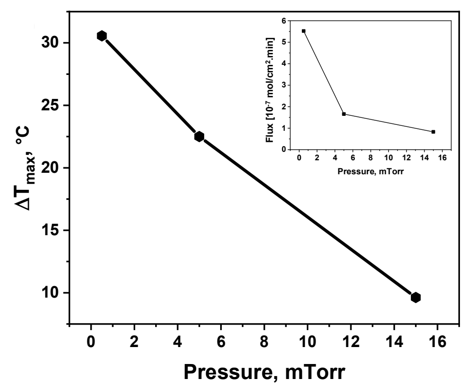
Fixed argon pressure: p_{Ar} = 5 mTorr





Fixed sputter power: P = 80 W





The liquid temperature increases at a rate up to 1°C/min.

Heating scales linearly with deposition rate

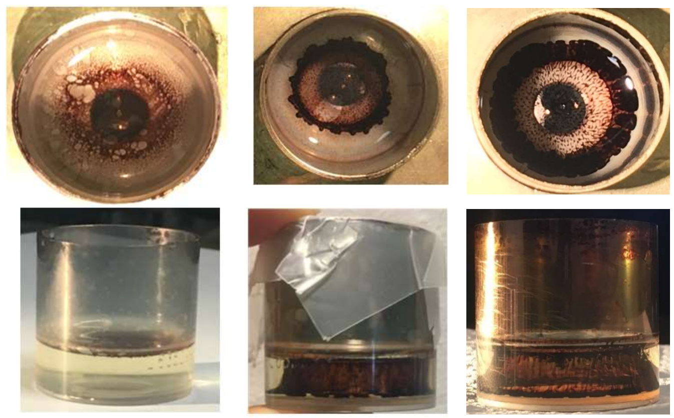
Temperature gradient in the solution may have implication

- in particle transport
- NP growth.

A.L. Thomann, S. Konstantinidis et al. *Surf. Coat. Technol.*, *377*, 124887 (2019).

Effect of the deposition time : Sputtering gold onto castor oil

DC-MS | 2-inch gold target
Ar pressure: 0.5 mTorr
Working distance: 20 cm
Sputter power: 80 W
Flux: $(2.50 \pm 0.46) \cdot 10^{-7}$ mol$\cdot$cm$^{-2}\cdot$min^{-1}



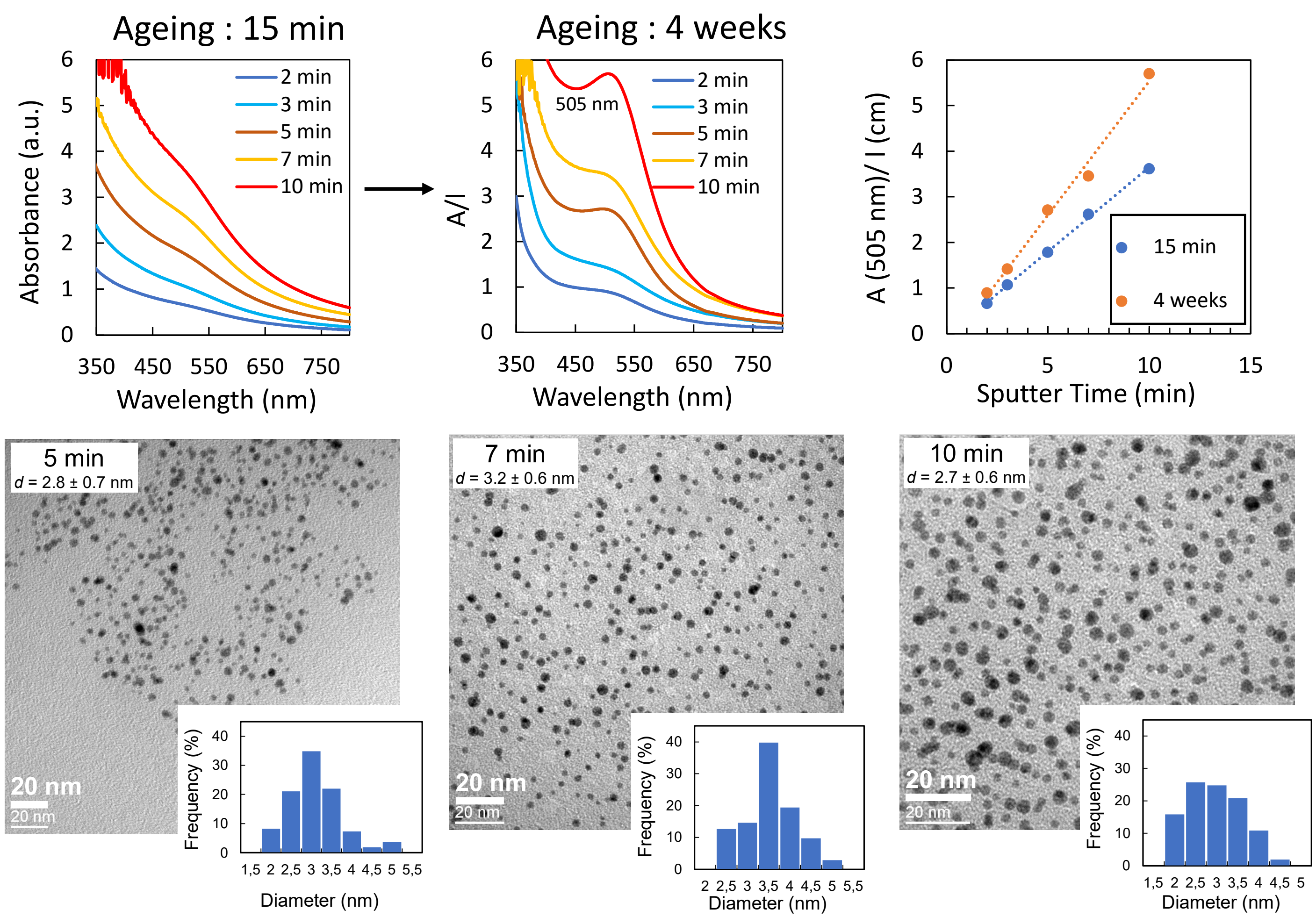
2 min | 5 min | 10 min

Deposition time allows controlling NP concentration

Homogeneous solution obtained after stirring

Sergievskaya A, S. Konstantinidis et al, *Front. Nanotechnol.* **3**:(2021)

Effect of the deposition time : Sputtering gold onto castor oil



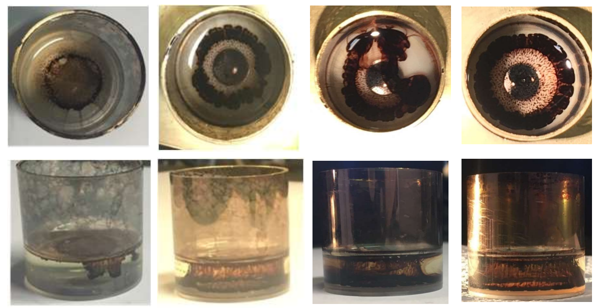
No influence of the deposition time on the size

Au-NP show secondary growth process

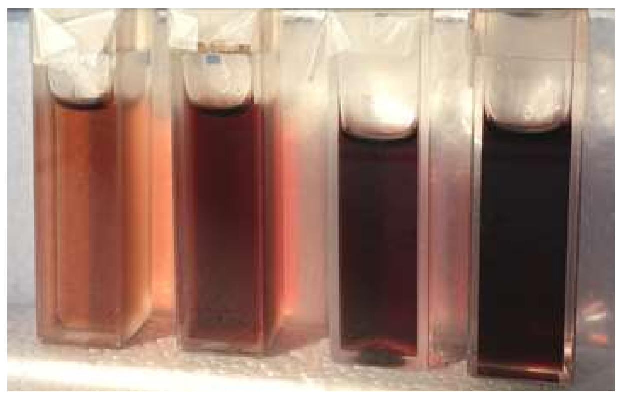
NPs reach a ~2.7 nm size

Effect of sputter power : Sputtering gold target onto castor oil

DC-MS | 2-inch gold target
Ar pressure: 0.5 mTorr
Working distance: 20 cm
Deposition time: 10 min



20 W 40W 60W 80W



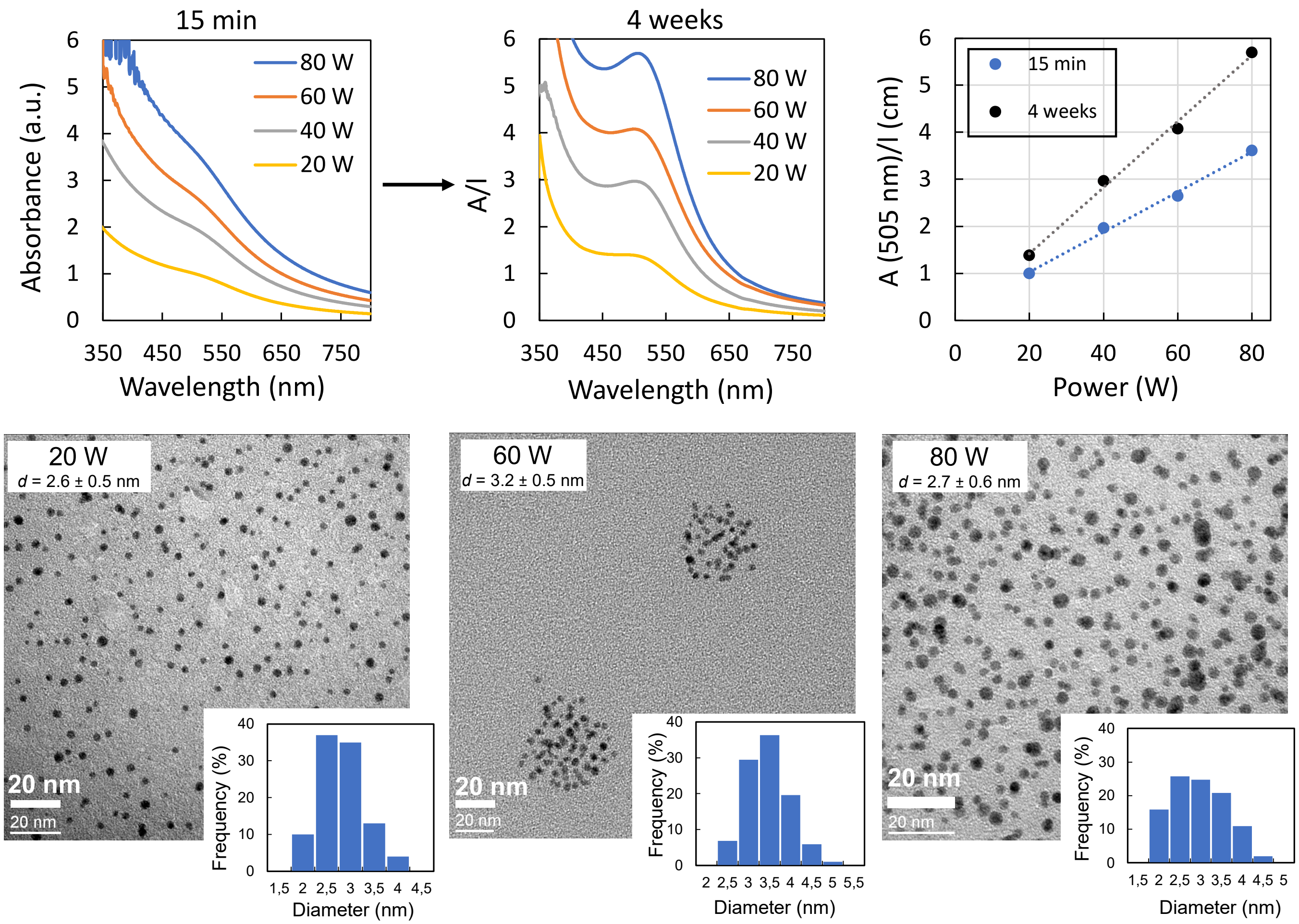
Sputter power controls the deposition flux, and allows controlling NP concentration

Homogeneous solution obtained after stirring

NP reach a ~2.5 nm size

A. Sergievskaya, S. Konstantinidis et al, *Front. Nanotechnol.* **3**:(2021)

Effect of sputter power : Sputtering gold target onto castor oil

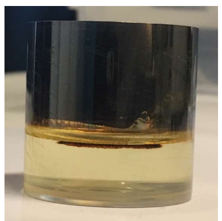


No influence of the deposition time on the size

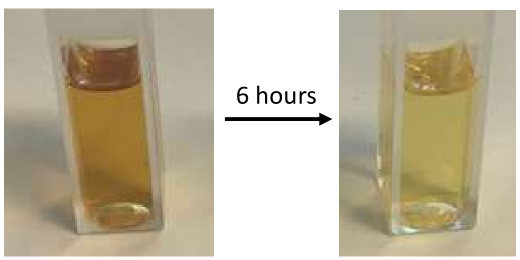
Au-NPs show secondary growth process

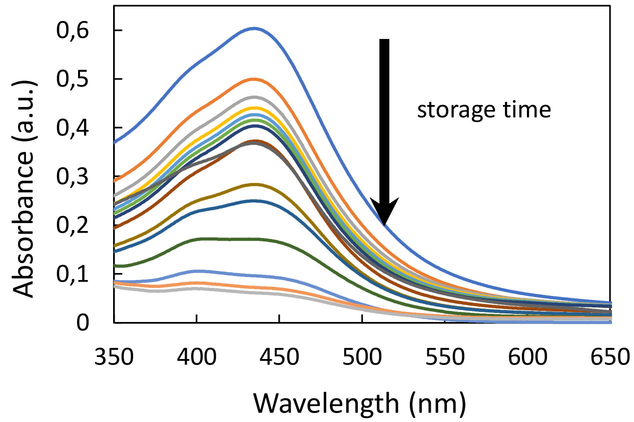
NPs reach ~2.7 nm size

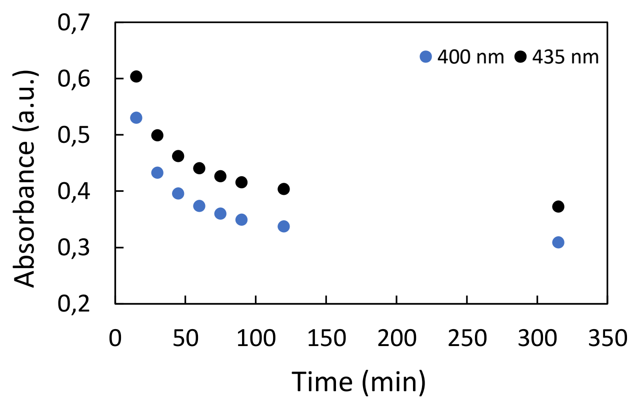
Sputtering silver onto castor oil,
A slightly different story

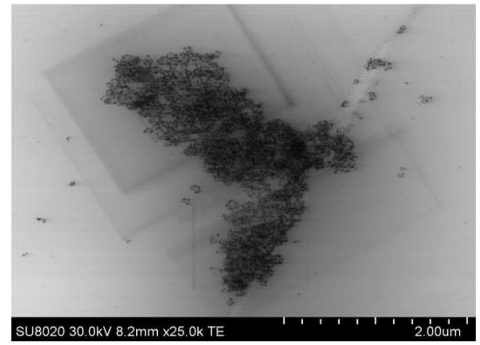


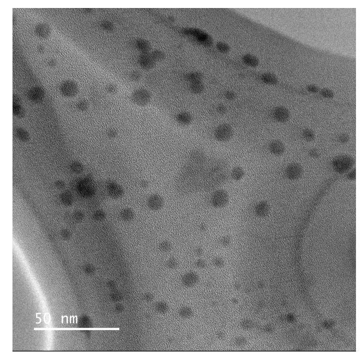
DC-MS | 2-inch siler target
0.5 mTorr, 20 cm, 80 W, 3 min
$\Phi = (0.6 \pm 0.1) \cdot 10^{-7}$ moles/cm$^2\cdot$min











8.1 nm ± 5.0 nm.
TEM image 8 months after preparation.

Ag-NPs re bigger than the Au-NPs grown in identical conditions

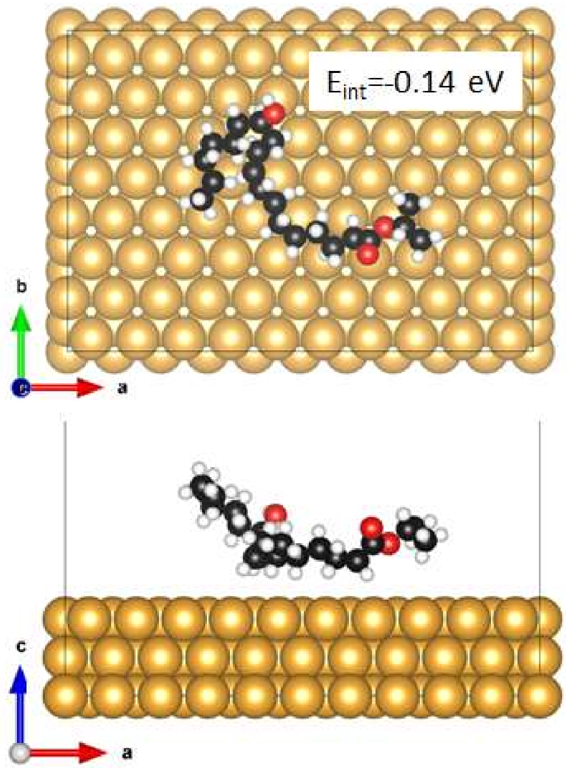
Unstable colloïdal suspension

A. Sergievskaya, S. Konstantinidis et al,
Colloids Surfaces A Physicochem. Eng. Asp. **615**:126286 (2021)

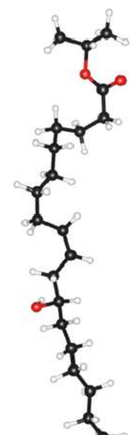
Stability of nanoparticles in castor oil: Interaction energy calculations

$$E_{int} = E_{surf/CO} - [E_{CO} + E_{surf}]$$

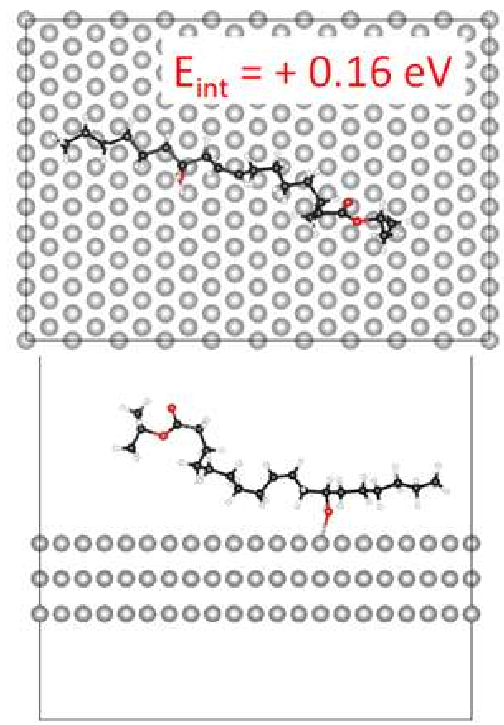
GOLD



1/3 of triglyceride of ricinoleic acid



SILVER

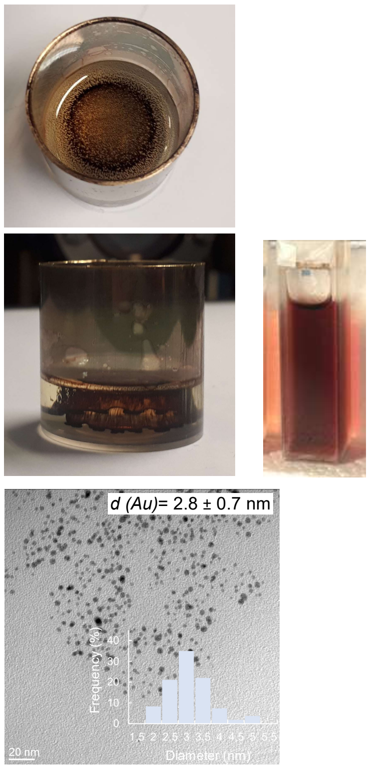


Efficient stabilization for Au,
Weak stabilization for Ag

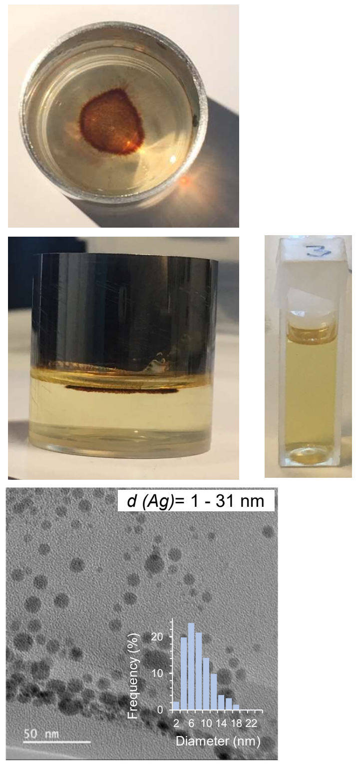
Influence of the liquid – NP interaction on the NP final size

Different metals, different colors, different issues

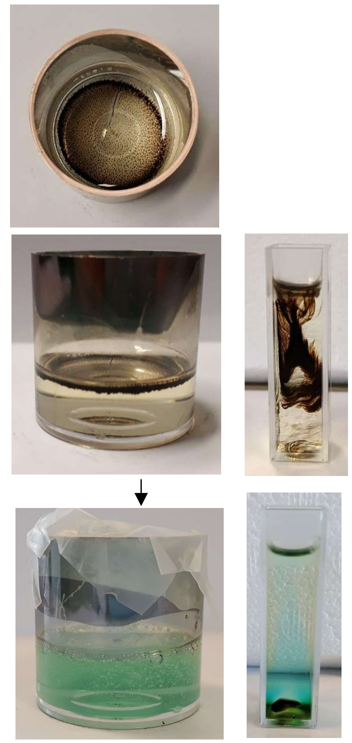
GOLD

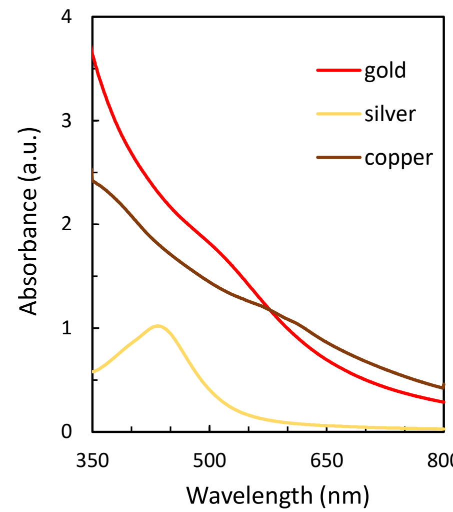


SILVER



COPPER



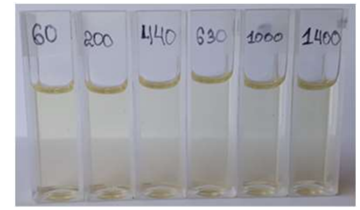


A. Sergievskaya, S. Konstantinidis et al, *Colloids Surfaces A Physicochem. Eng. Asp.* **615**:126286 (2021)

A. Sergievskaya, S. Konstantinidis et al, *Front. Nanotechnol.* **3**:(2021)

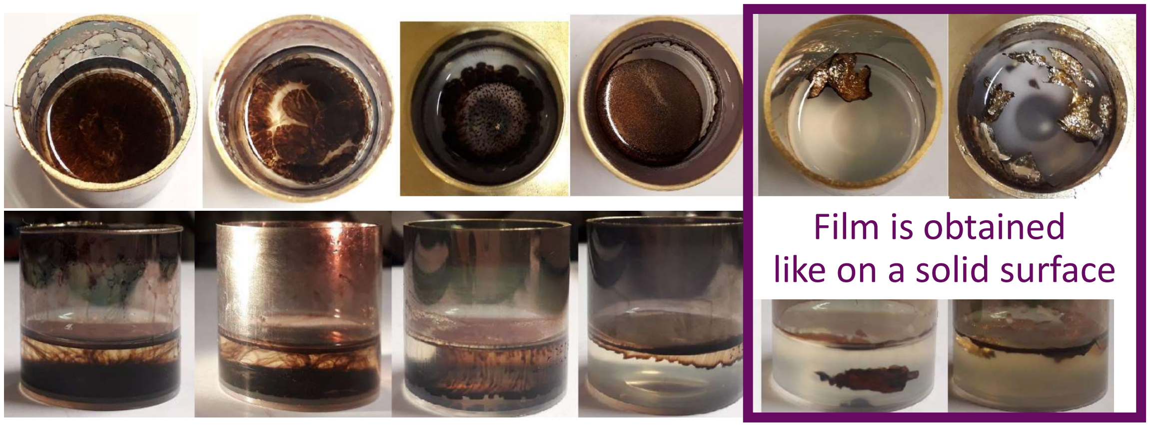
Effect of host liquid viscosity

DC-MS, 2-inch gold target, p_{Ar}= 0.5 mTorr, 20 cm, P=80 W, t_s=5 min,
Liquid : **polymerized* rapeseed oil** plasma treatment prior sputtering



Surface tension: ~ 32.7 mJ · m^{-2}

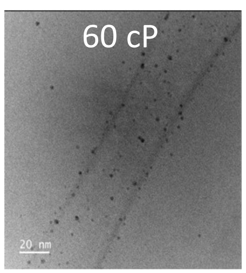
Viscosity (cP) **60** **200** **440** **630** **1000** **1400**



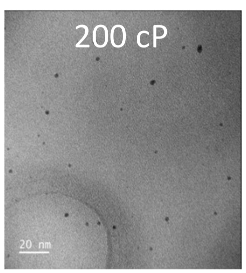
XRD: Au films

d_{Au} (1000 cP) = 10 ± 1 nm

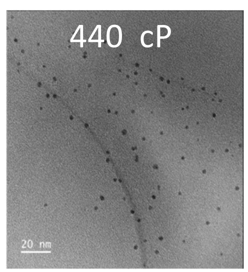
d_{Au} (1400 cP) = 11 + 1 nm



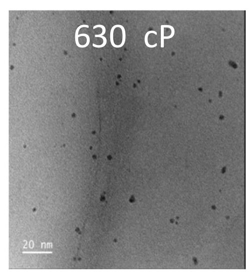
2.14±0.69 nm



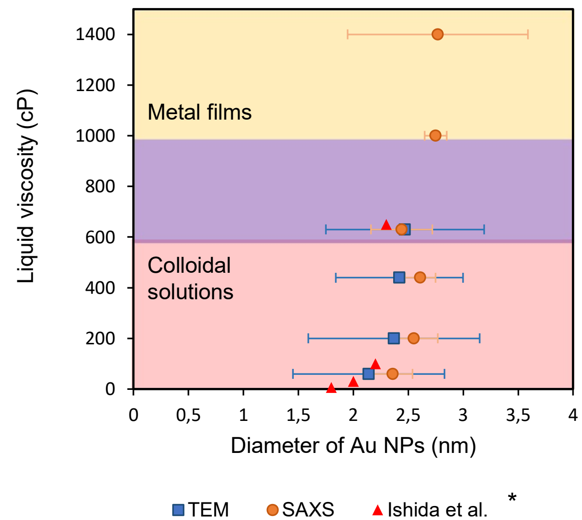
2.37±0.78 nm



2.42±0.58 nm



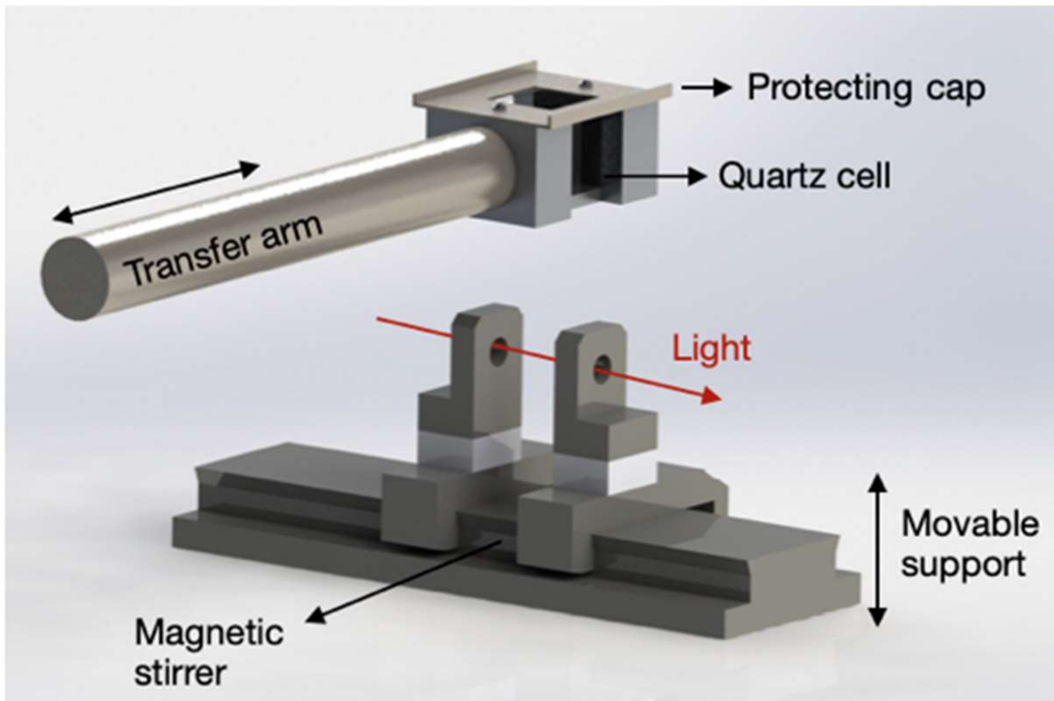
2.47±0.72 nm



* Ishida Y, Udagawa S, Yonezawa T (2016)
Colloids Surfaces A Physicochem Eng Asp 498:106–111.

A. Sergievskaya, S. Konstantinidis et al, PCCP, *accepted*

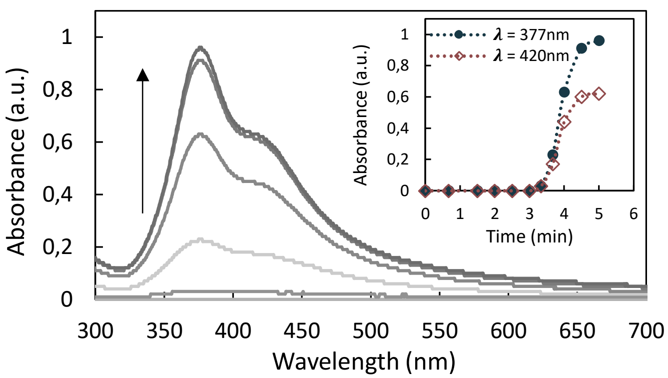
Analyzing the liquid during sputtering, Operando UV-Vis spectrophotometry

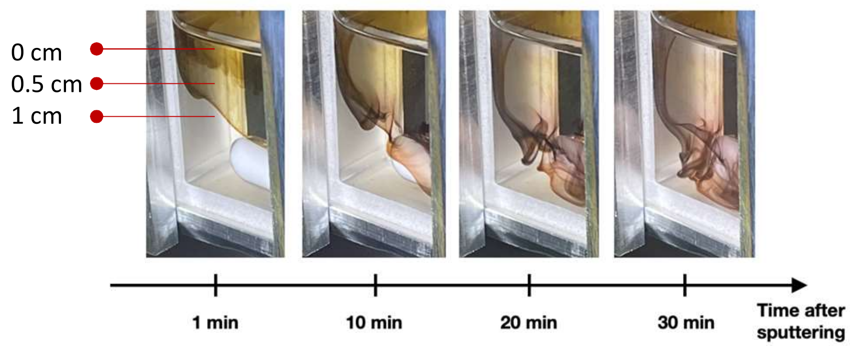


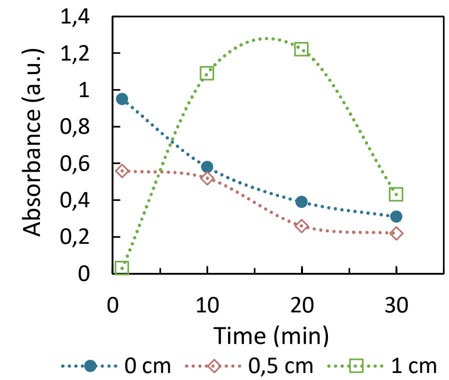
S. Konstantinidis, F.-E. Bol, A. Sergievskaya, et al. "Operando absorption spectrophotometry during sputtering onto liquids", *in progress*

Growth and aggregation of Ag-NPs in silicon oil

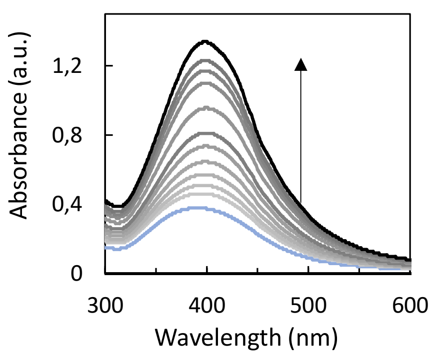
without stirring

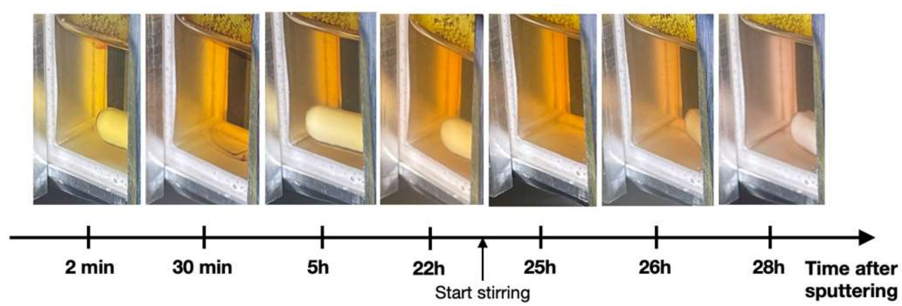




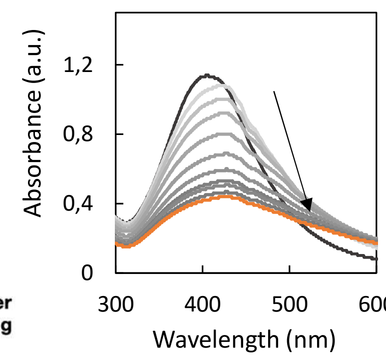


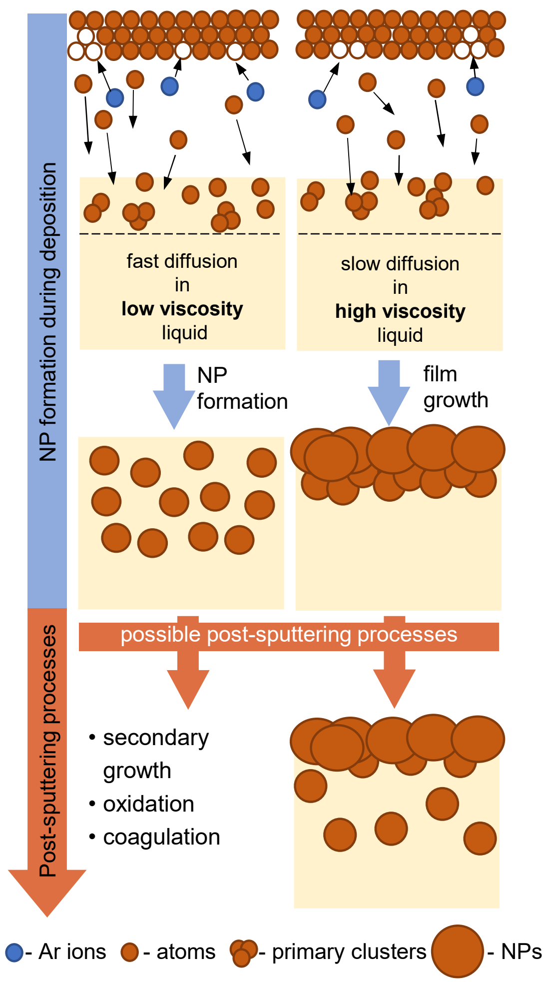
with stirring





Stirring promotes aggregation





To conclude

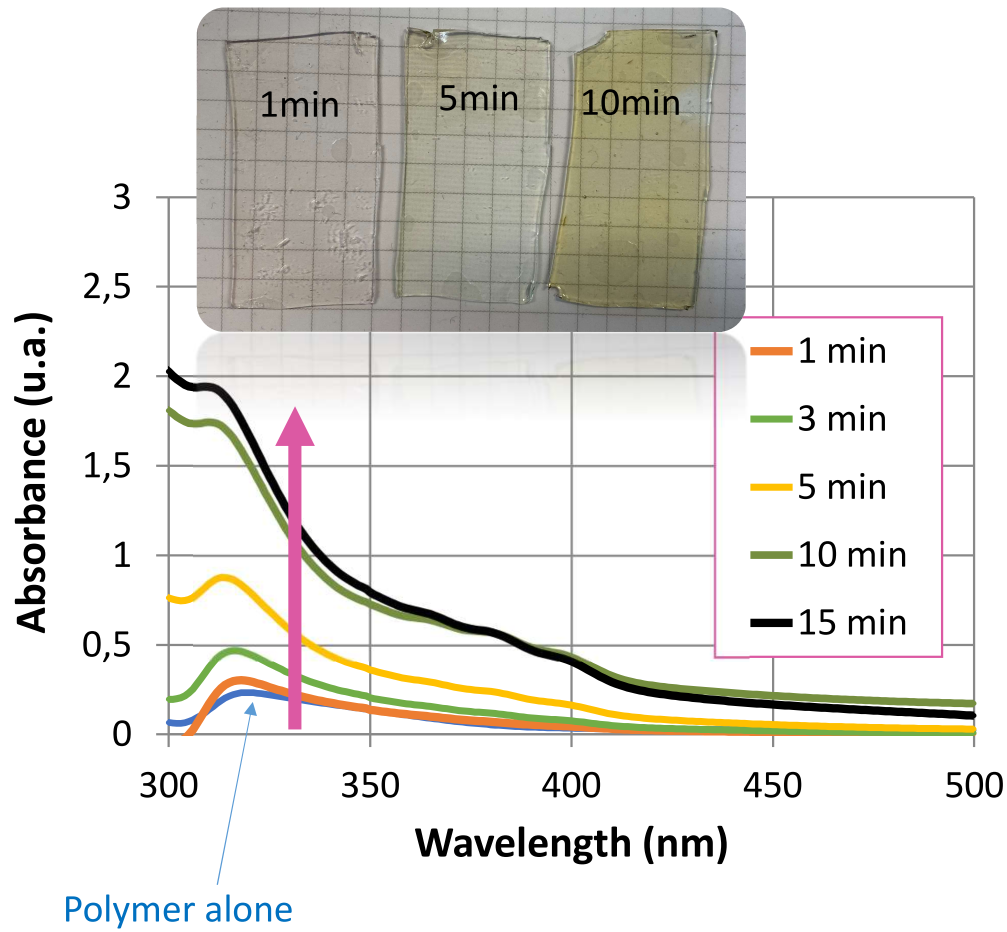
1. Sputtering onto Liquids (SoL) allows obtaining colloidal solutions of small NPs (and thin metal films).
2. Physico-chemical characteristics of the host liquid and the NP chemistry determine the properties of the final product for the similar deposition conditions.
    - Situation might be different if the plasma source is changed e.g., HiPIMS plasma are used

- Stirring during the deposition allows to homogenize the solution but also promotes secondary processes as aggregation or oxidation.

- There are still a lot to understand and explore !

Beyond the synthesis of nanoparticles

…Towards the elaboration of flexible **polymer-NPs composites** by sputtering atoms onto liquid monomers (e.g., PEG)



V. Jauquet, J.- M. Raquez, J. Odent, SMPC lab, UMONS