11TH INTERNATIONAL CONFERENCE ON HIPIMS

HIPIMS 2021

SPUTTERING ONTO LIQUIDS FOR NANOPARTICLE SYNTHESIS

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Advantages of sputtering onto liquids

1. **Flexibility**

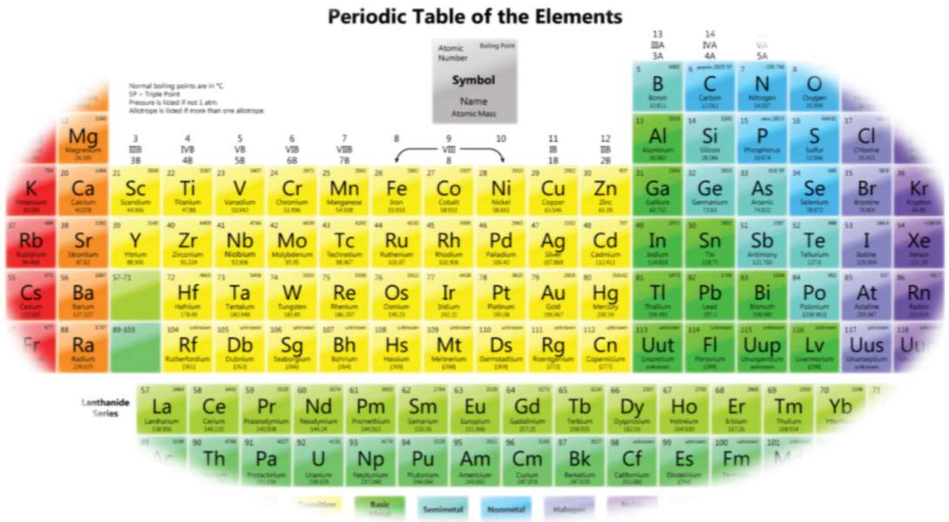
   Large variety of elements can be sputtered

2. **Safety**

   NP « stored » in the host liquid

3. **Purity**

   Chemical reactants and by-products are avoided

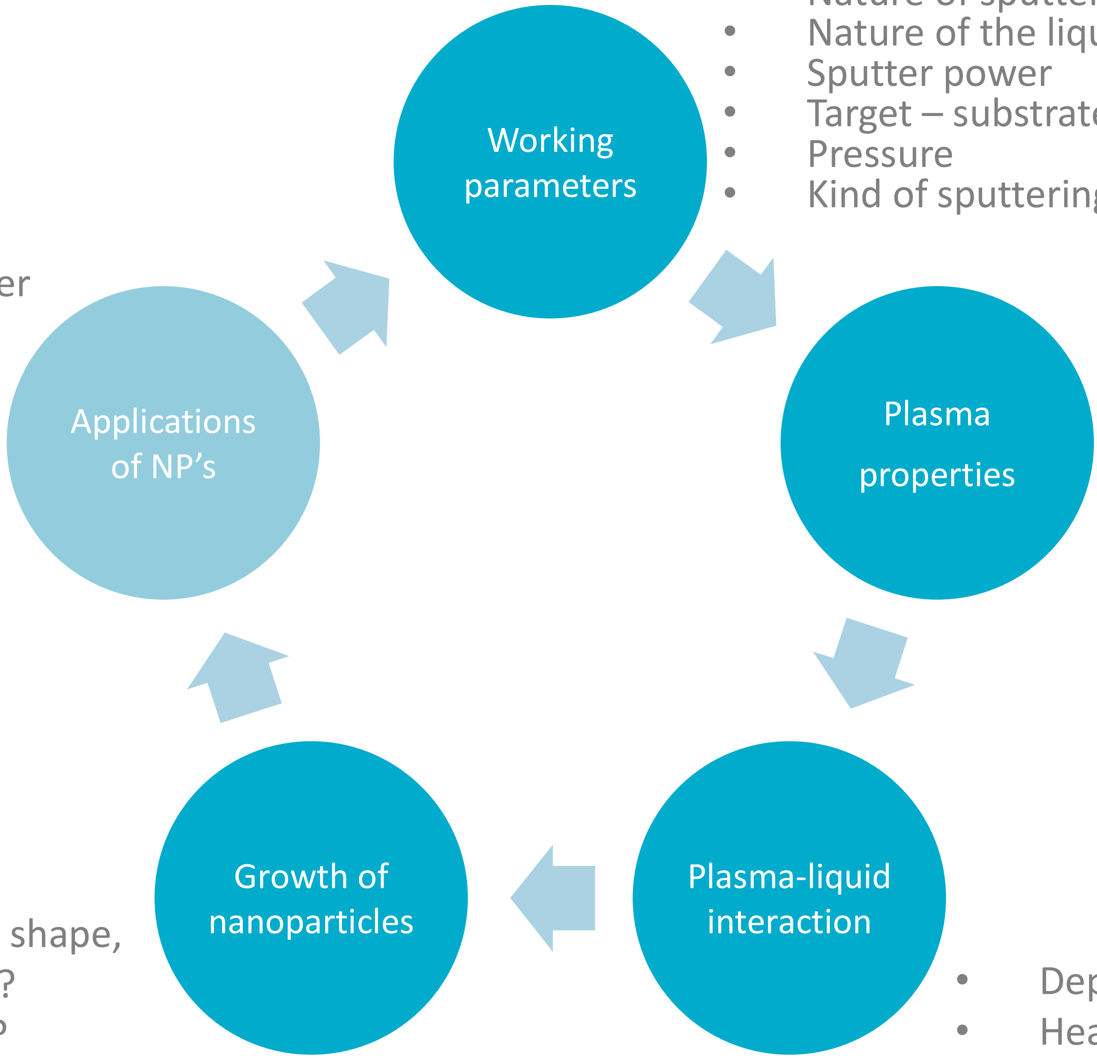


$+ O_2 / N_2 / \dots$

Our goal

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

- Collaboration with other research groups

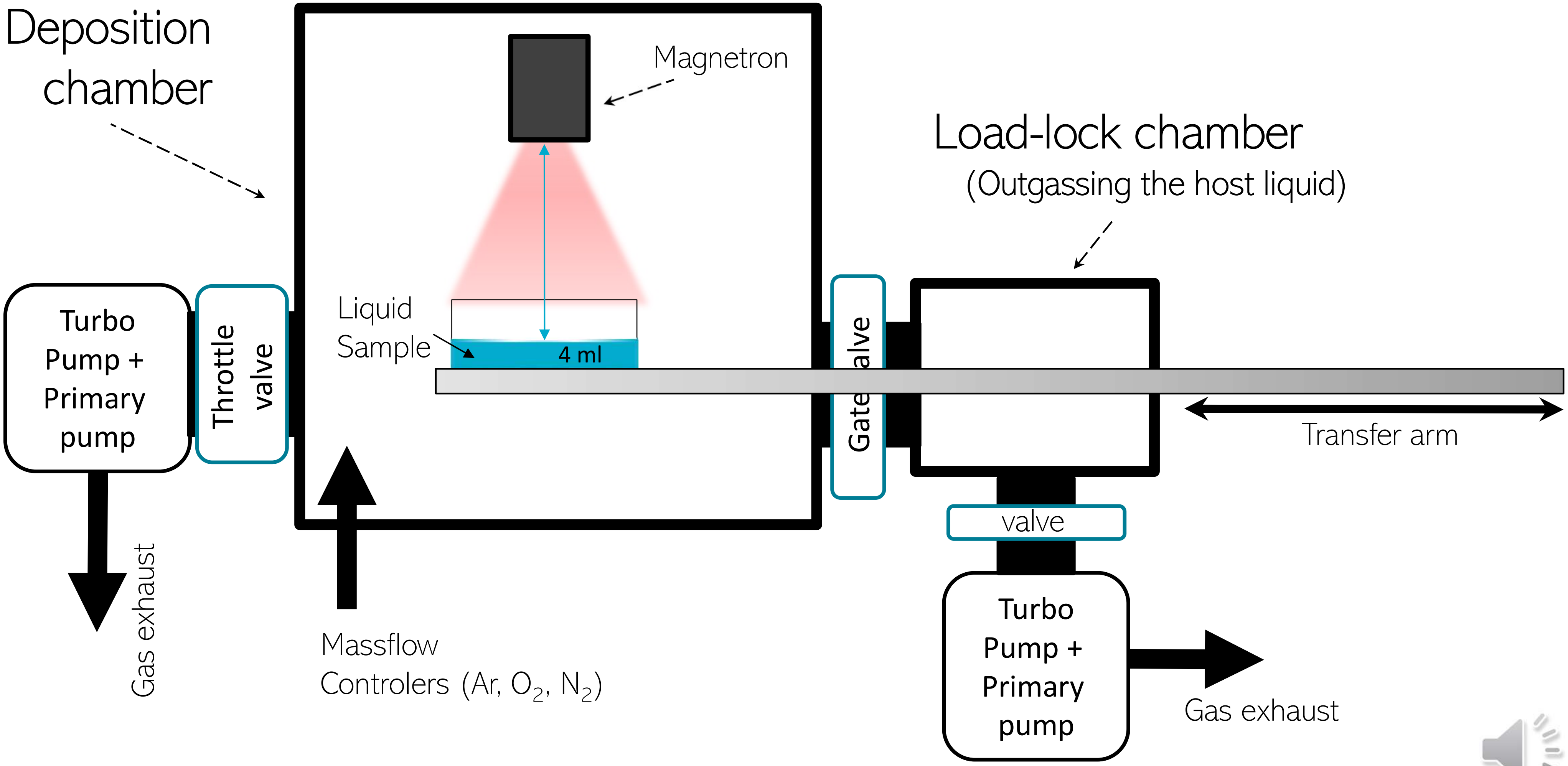


- Particle fluxes
- Kinetic energies

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

- Deposition rates
- Heating of the liquid
- Liquid chemistry

Experimental set-up

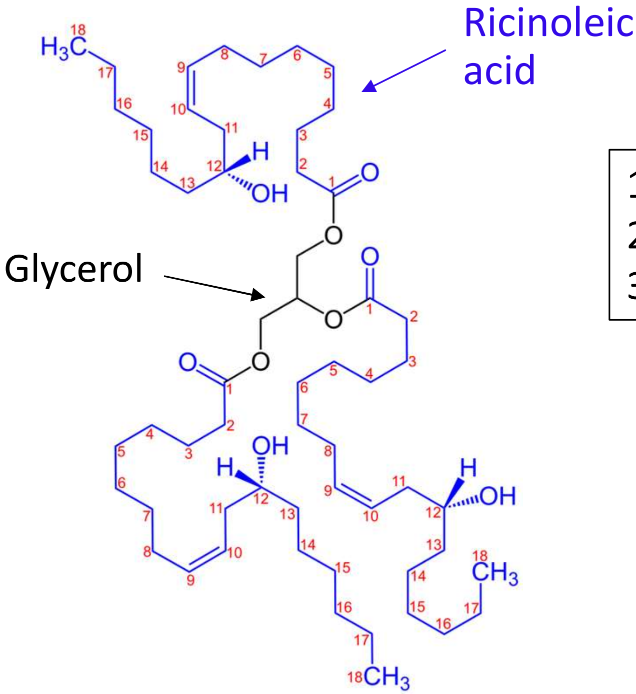


Castor oil as a host liquid

Ricinus communis

Castor beans

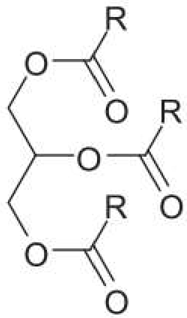
Ricinoleate



1. Withstand vacuum
2. Low toxicity
3. Low cost

Castor oil = mixture of triglycerides
- ricinoleate ~ 90 %
- oleate ~ 7%
- linoleate ~ 3%

Generic Triglyceride



Influence of the working parameters on the NP properties

Varying parameters are:

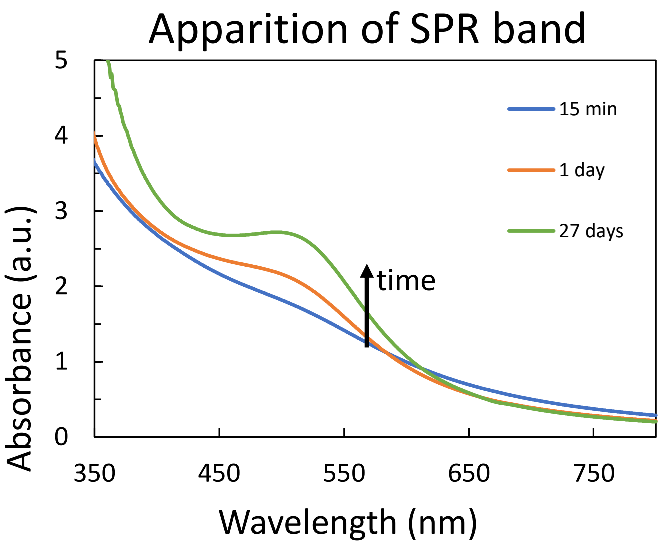
1. Sputter power
2. Deposition time
3. Kind of sputtering discharge (DCMS vs. HiPIMS)
4. Viscosity of the host liquid
5. Nature of the sputtered metal (Au, Ag, Cu)

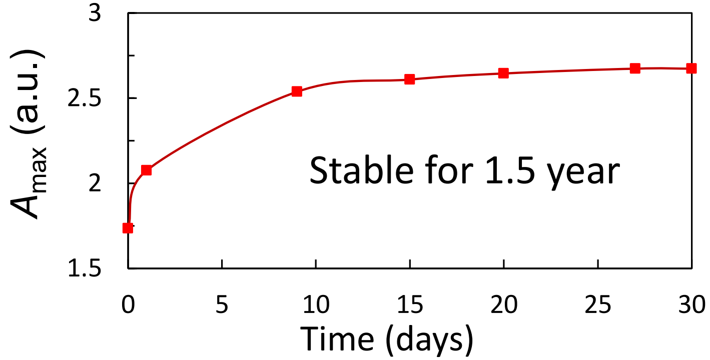
TEM and UV-Vis spec. provide info about

1. The size of the NP
2. The ageing/stability of the NP solutions

DC-MS of gold onto castor oil, a first look

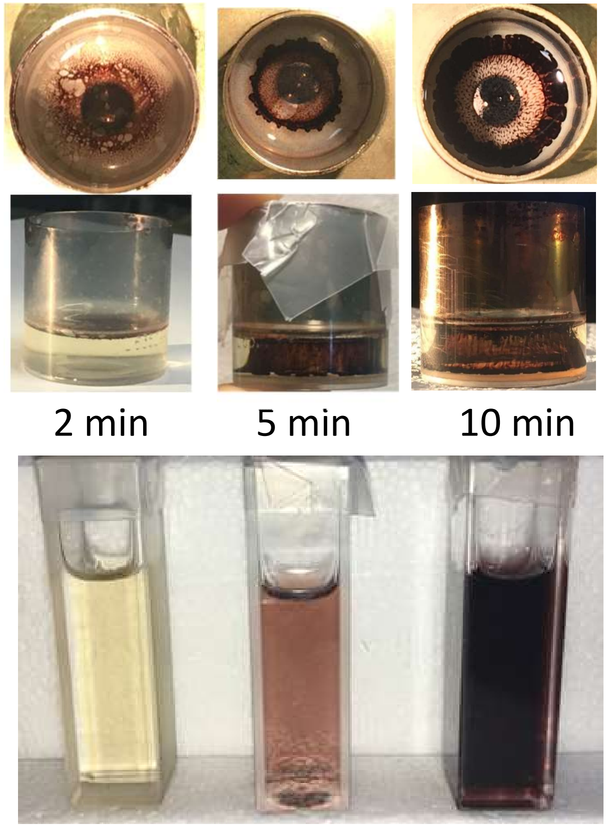
P_{Ar} = 0.5 mTorr, T-S dist.: 20 cm, 5 min, 80 W → Flux of metal atoms : $\Phi = (2.5 \pm 0.5) \cdot 10^{-7}$ mol·cm^{-2}·min^{-1}





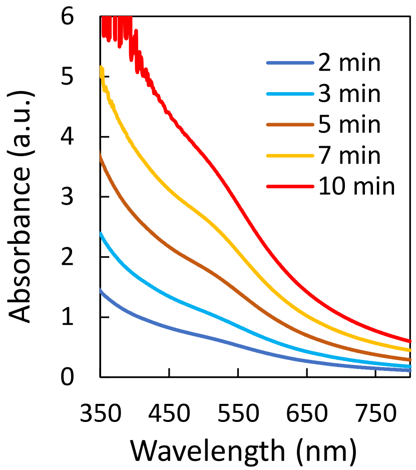
- NP continue to grow for a few days after sputtering
- NP solutions are stable for a very long time

Effect of sputter time

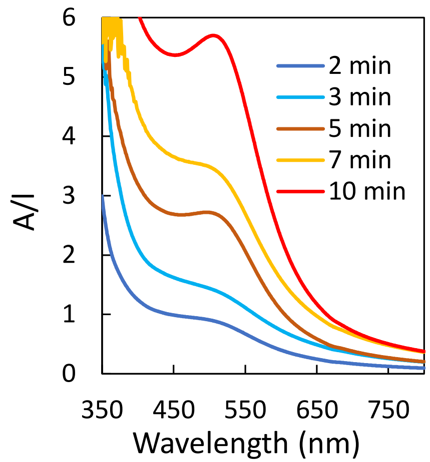


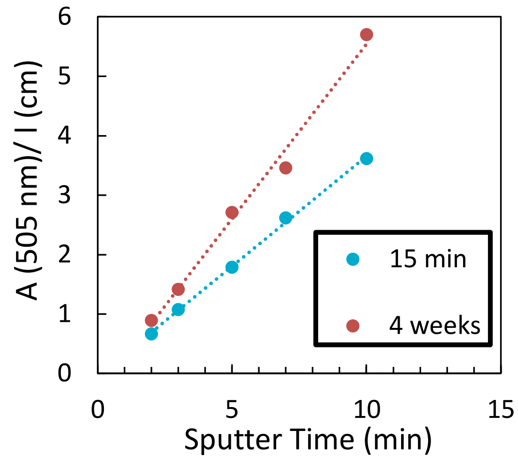
Ageing of the NP solutions

15 min after sputtering

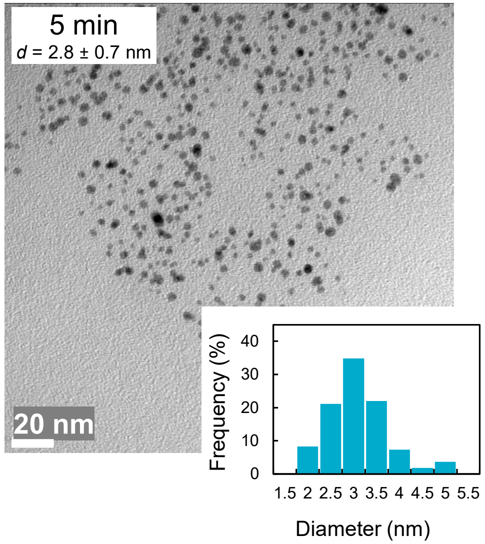


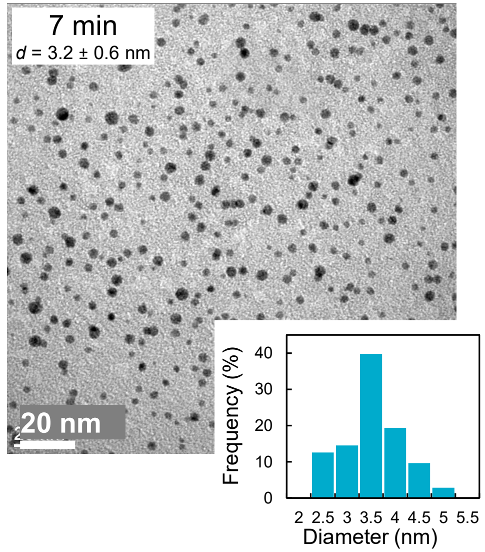
4 weeks after sputtering

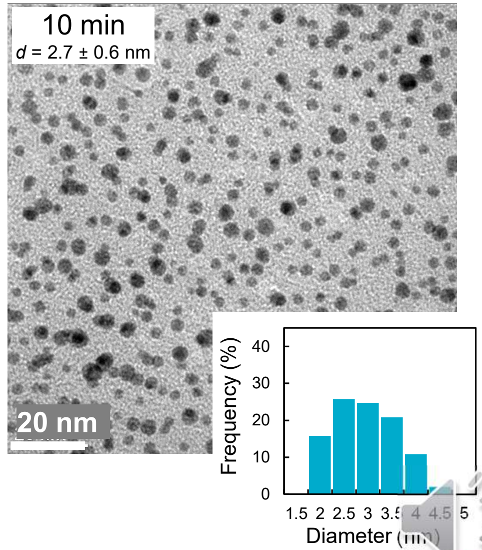




TEM analysis after 6 months

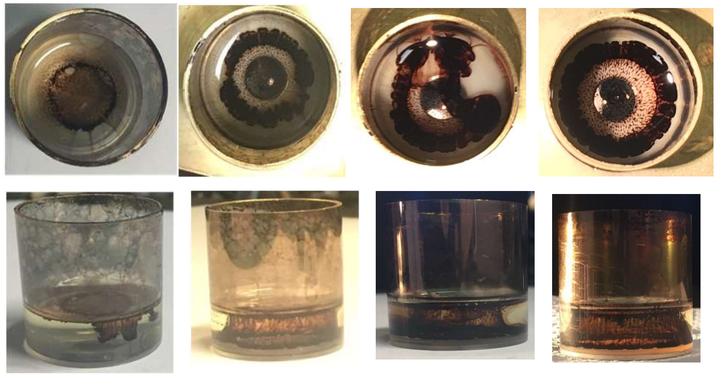






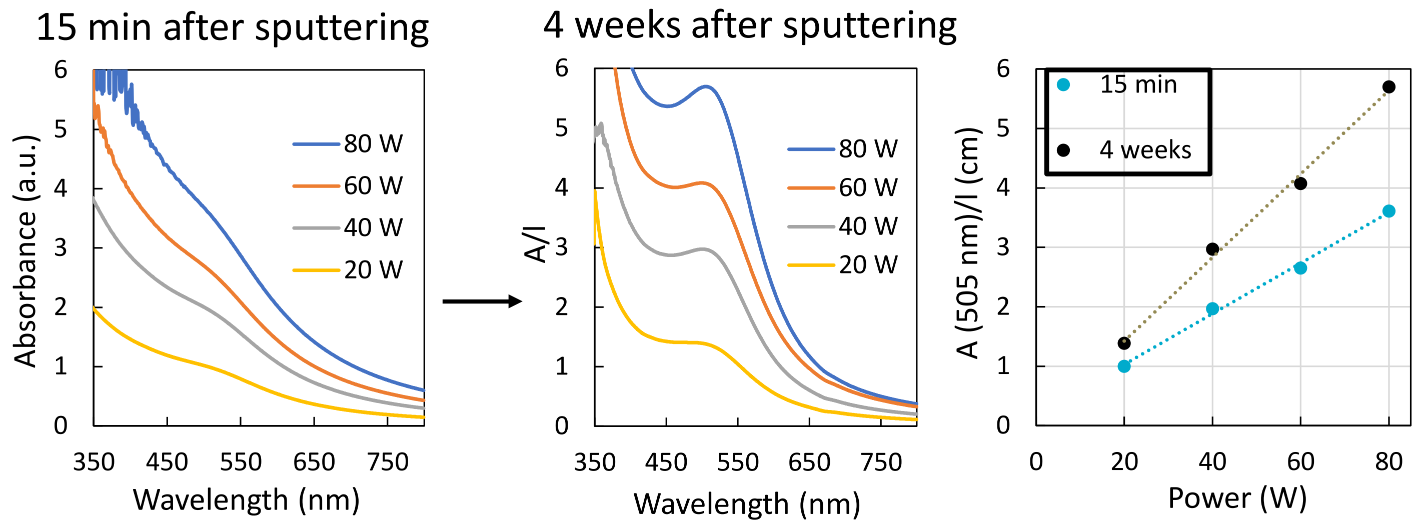
Effect of sputter power

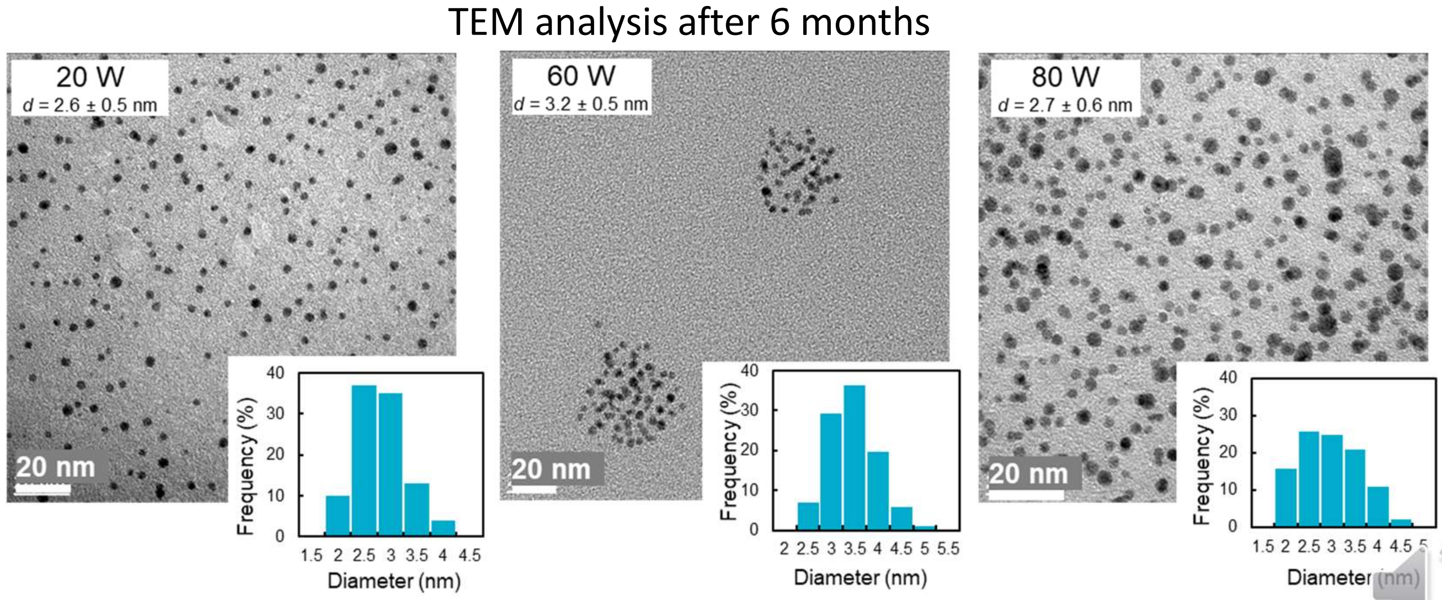
Sputter time: 10 min



20 W 40W 60W 80W

Ageing of the NP solutions





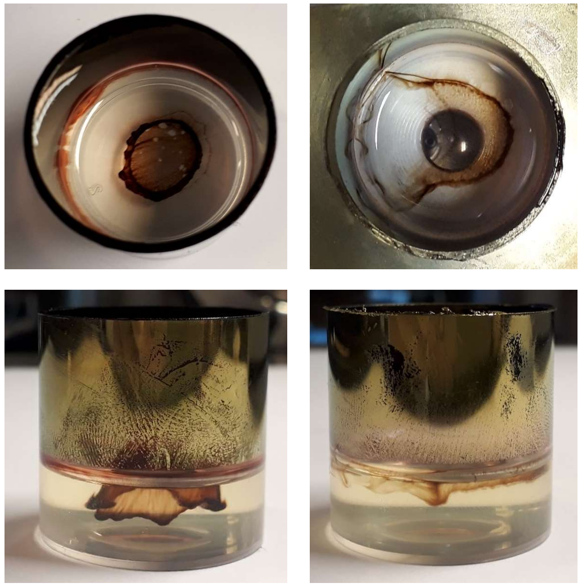
DC-MS *vs.* (unipolar) HiPIMS

P_{Ar} = 5 mTorr, 80 W, 10 min

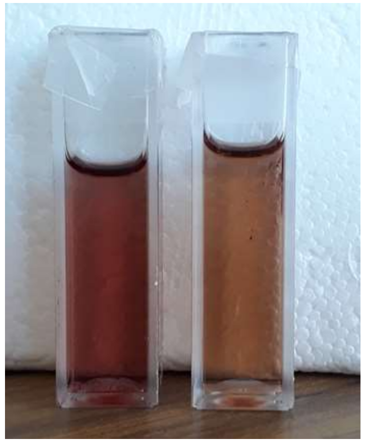
DC-MS:
Φ = $(1.8 \pm 0.2)\cdot 10^{-7}$ moles/cm^2·minute

HiPIMS:
T_{on} = 20 µs, I_{pk} = 0.3 A/cm^2, f = 800 Hz,
Φ = $(0.9 \pm 0.1)\cdot 10^{-7}$ moles/cm^2 min

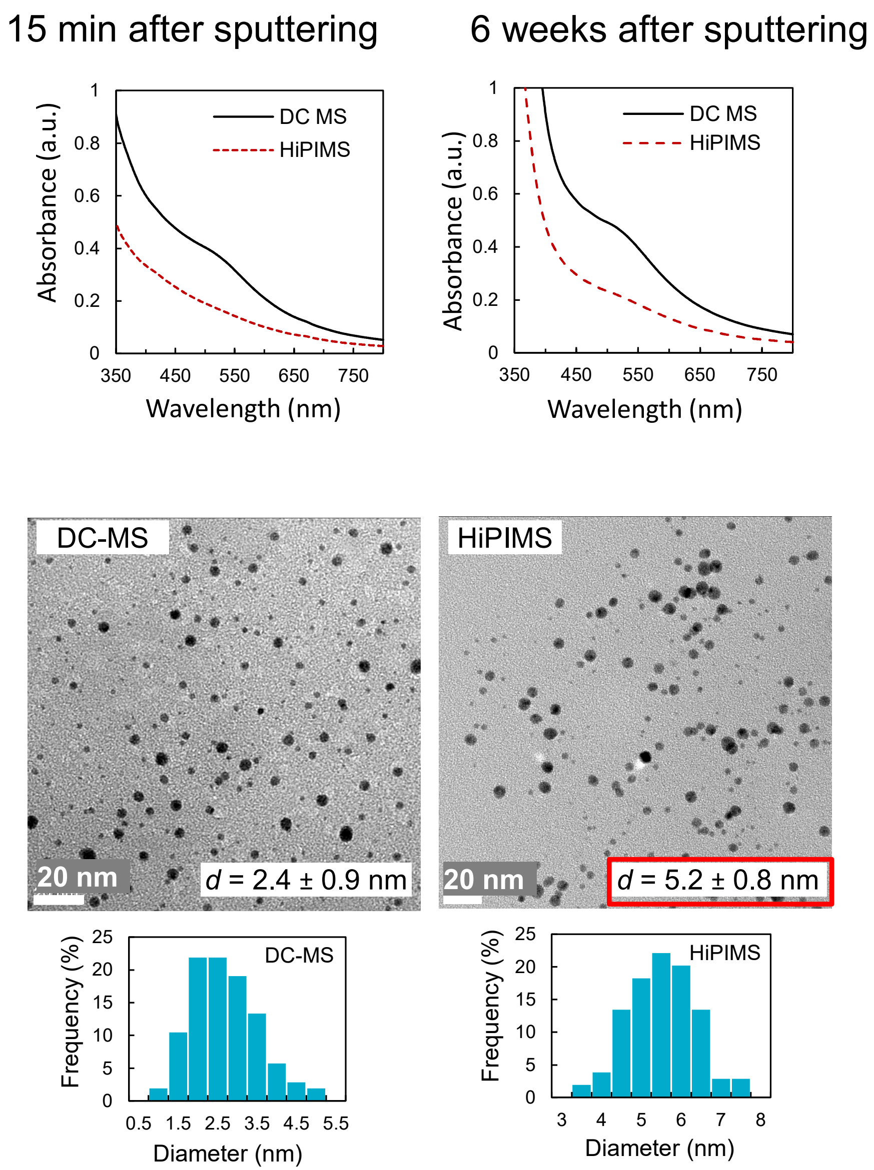
DC-MS HiPIMS



DC-MS HiPIMS



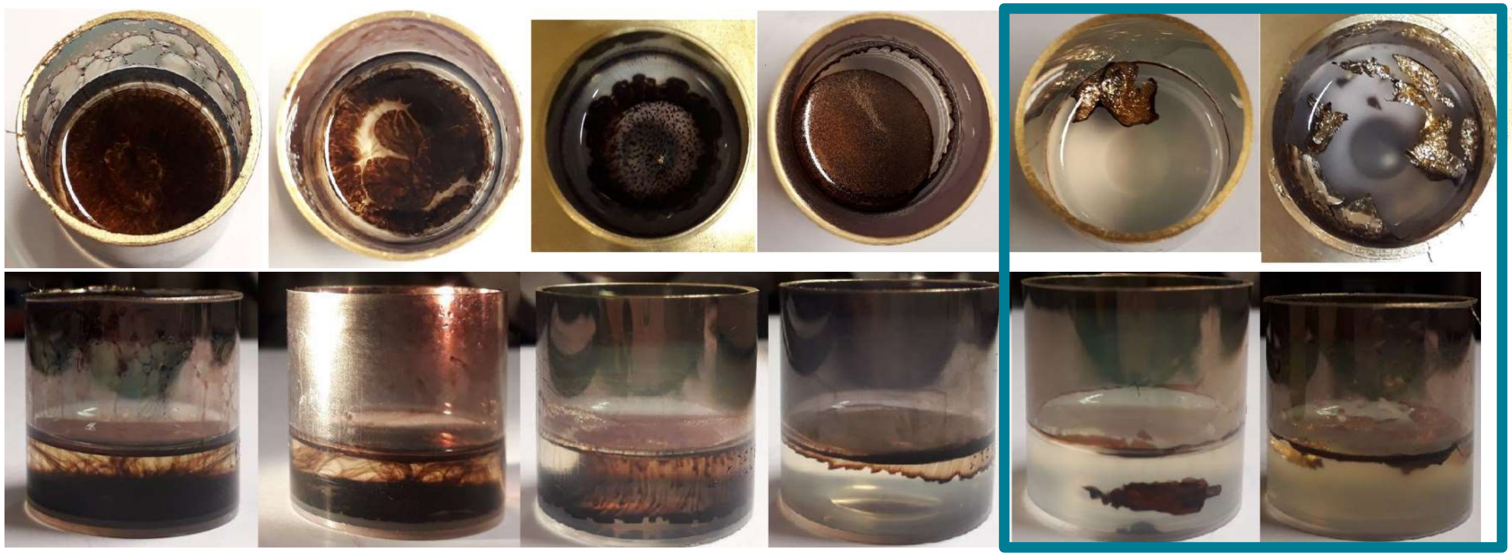
Ageing of the NP solutions



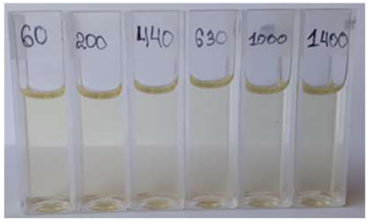
Effect of host liquid viscosity

0.5 mTorr, 20 cm, 80 W, 10 min, Liquid : **polymerized* rapeseed oil**
* Plasma treatment prior sputtering

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



Surface tension
~ 32.7 mJ · m^{-2}

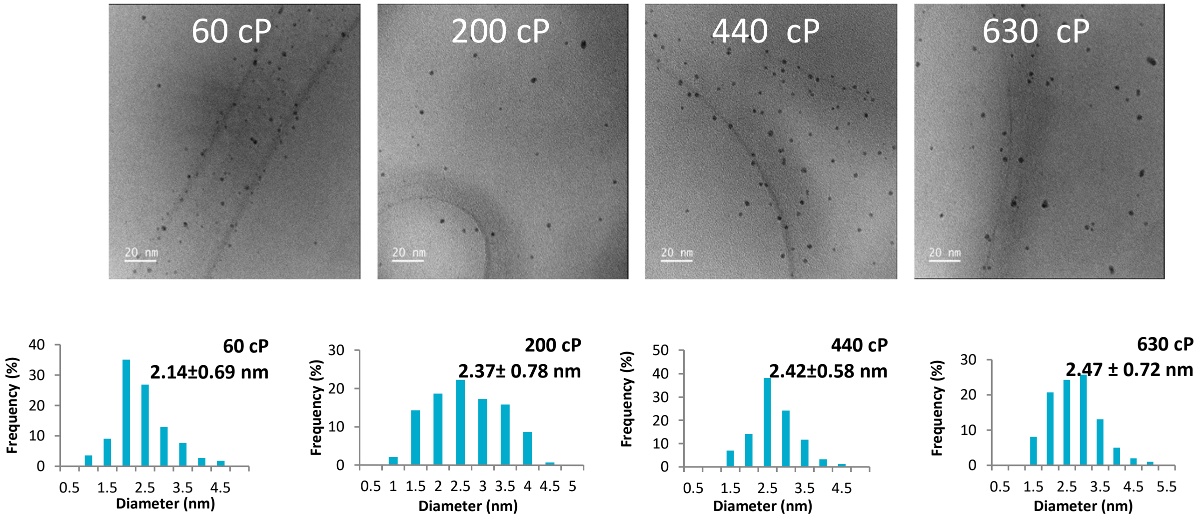


Viscosities (cP)

- Castor oil = 700 cP (35.1 mJ m^{-2})
- Water = 0.9 cP
- Honey ~ 2000 – 10 000 cP

Film is obtained
like on a solid surface

Effect of host liquid viscosity



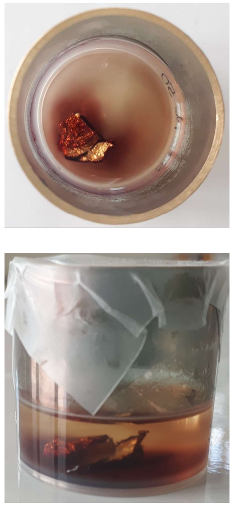
No TEM data for high viscosity liquids
Impossible to remove the liquid from the TEM grid

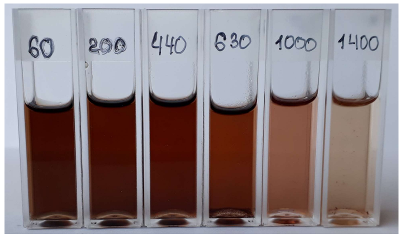
Ageing of the solutions

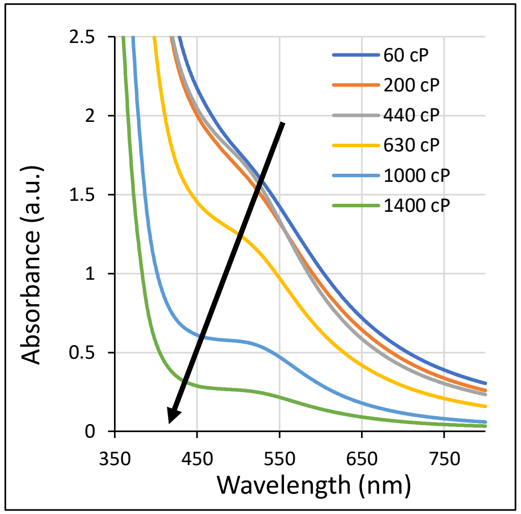
0.5 mTorr, 20 cm, 80 W, 10 min, substrate : polymerized rapeseed oil

5 months

Partial dissolution







At higher viscosity

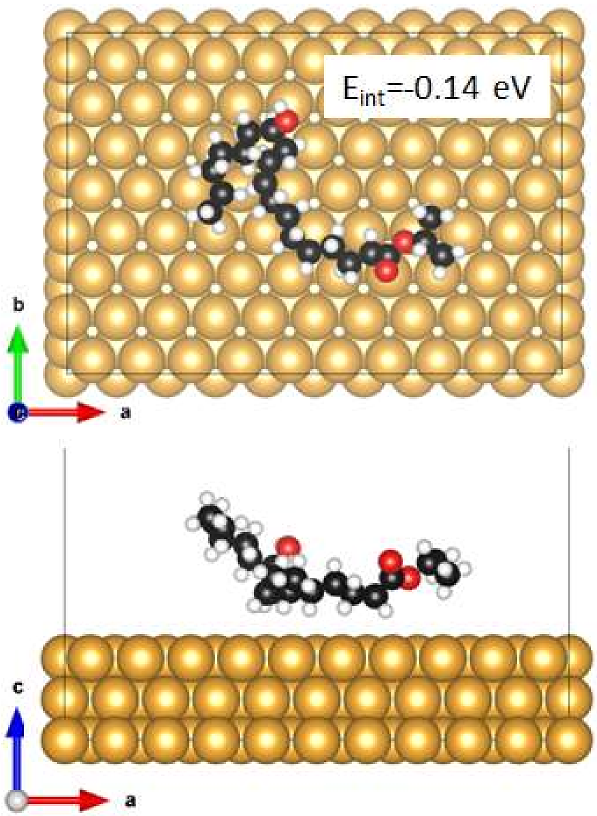
- Better definition of the SPR band
  → Bigger NPs ?
- But lower concentration of NP

What if we sputter silver onto castor oil ?

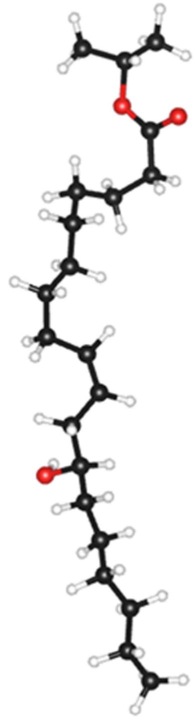
Metal surface – liquid interaction energy

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

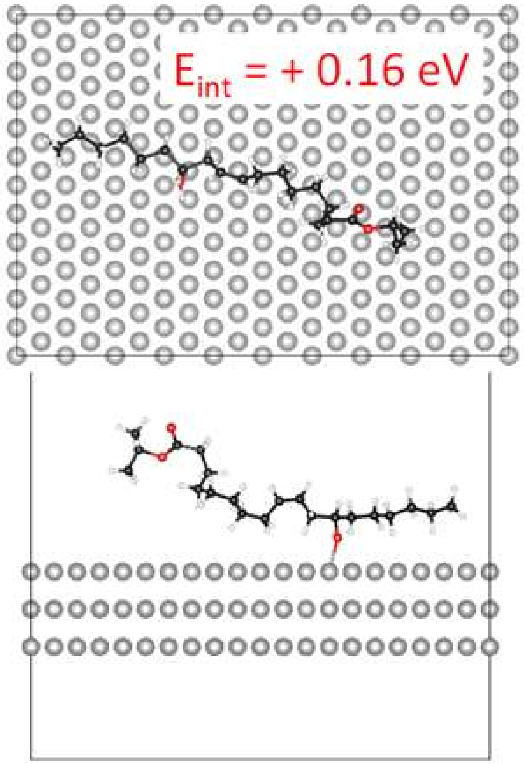
GOLD



1/3 of triglyceride
of ricinoleic acid



SILVER

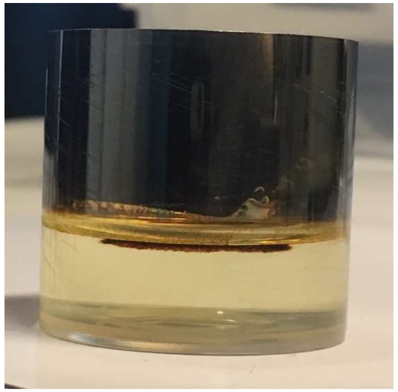


SK31

DC-MS of silver target onto castor oil

0.5 mTorr, 20 cm, 80 W, 3 min

$\Phi = (0.6 \pm 0.1) \cdot 10^{-7}$ moles/cm^2$\cdot$min

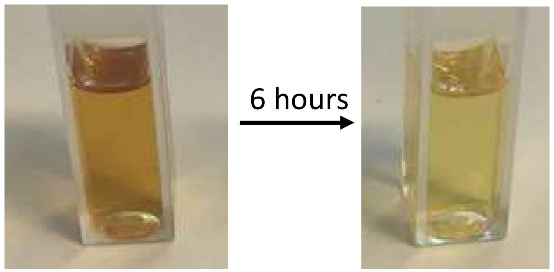


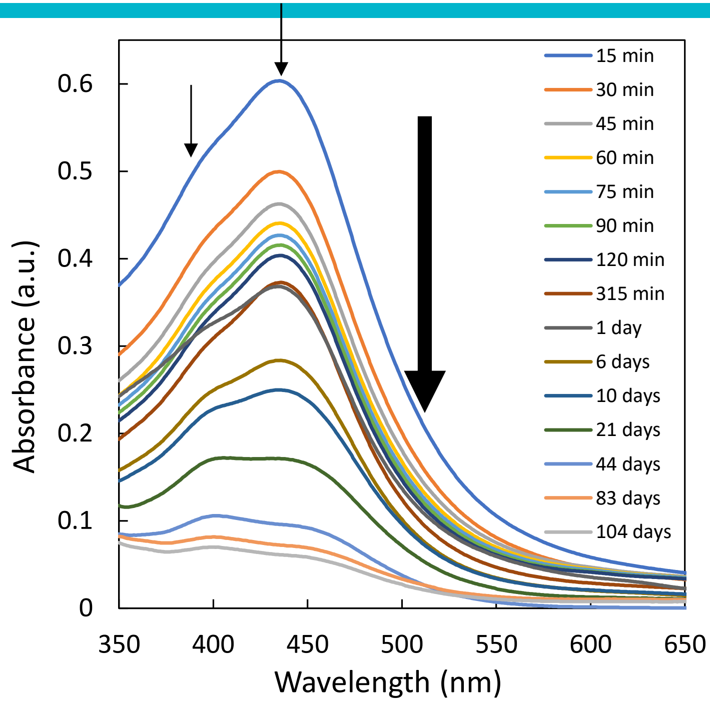
SK9 size distribution, cristalinity ?
Stéphanos KONSTANTINIDIS; 03-05-21

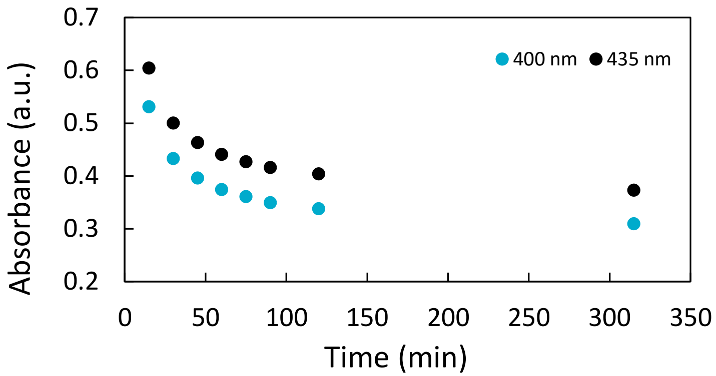
Ui16 There is no size distributions for these particlular images due to low quality. I used them to tell that particules aggregate in the castor oil and this is the reason of decrease in absorbance.
We have a lot of TEM images of silver NPs, including HiPIMS and bipolar HiPIMS with size distribution and data about crystallinity. I will send it to you.
Utilisateur invité; 07-05-21

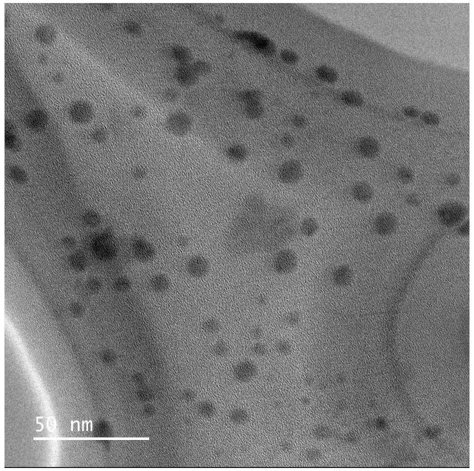
SK31 If you have the NP size distribution, it woul dbe great. THanks !
Stéphanos KONSTANTINIDIS; 20-05-21

Ageing of the Ag-NP solutions









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

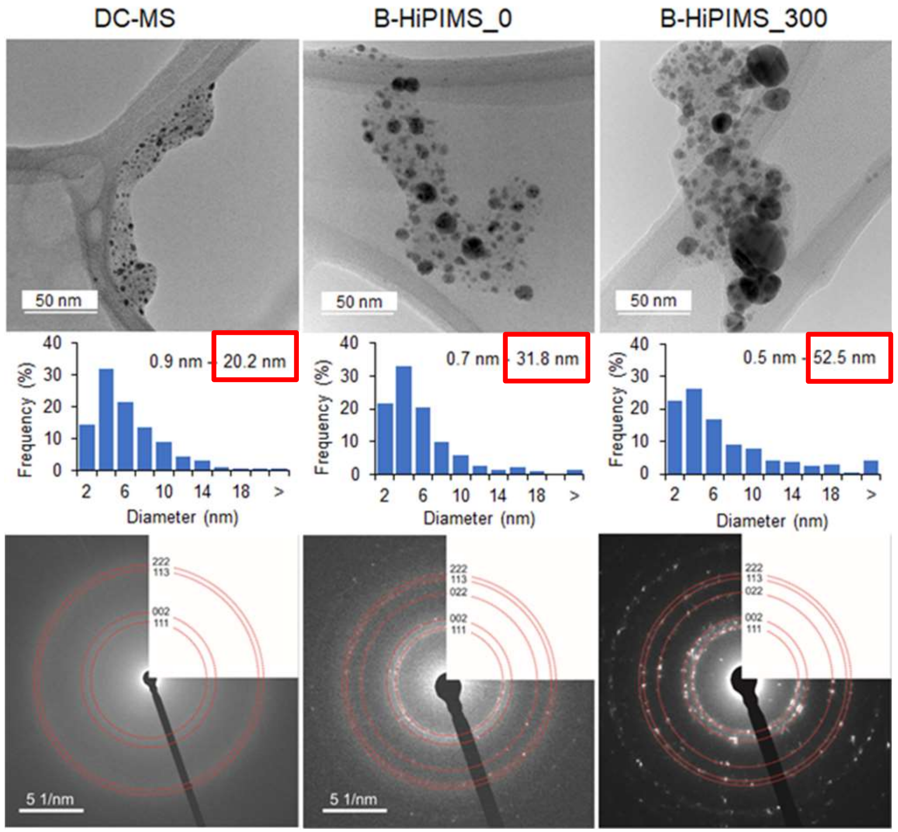
With time, Ag-NP aggregates due to low affinity for castor oil

DC-MS *vs.* Unipolar & Bipolar HiPIMS

P_{Ar} = 5 mTorr, 80 W, 10 min
Flux DC-MS: $(1.8 \pm 0.2)\cdot10^{-7}$ moles/cm^2 min

Flux HiPIMS: $(0.9 \pm 0.1)\cdot10^{-7}$ moles/cm^2 min
f = 800 Hz, $T_{ON,-}$ = 20 µs, I_{pk} = 0.3 A/cm^2

Flux B-HiPIMS: $(0.2 \pm 0.1)\cdot10^{-7}$ moles/cm^2 min
f = 800 Hz, $T_{ON,-}$ = 20 µs, I_{pk} = 0.3 A/cm^2
V_+ = +300V, $T_{ON,+}$ = 250 µs, $T_{+/-}$ = 10µs

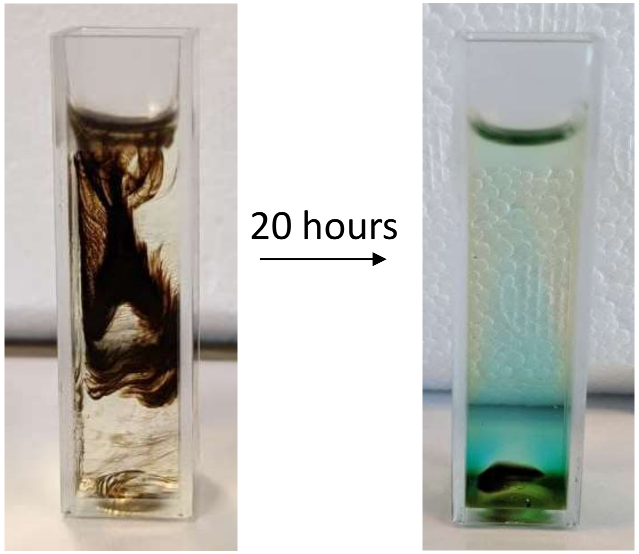


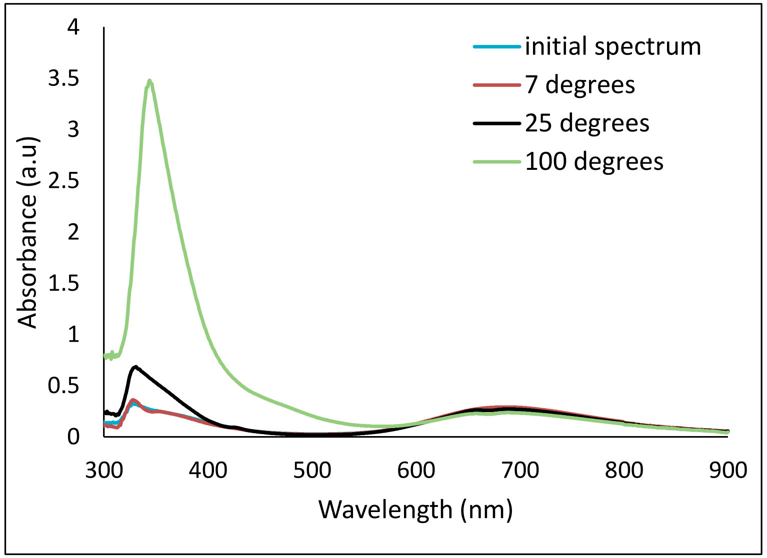
Number of particles larger than 20 nm

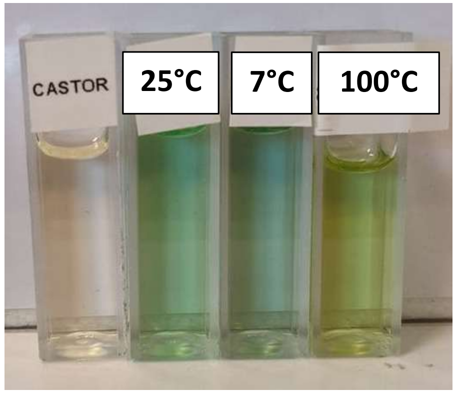
- 0.1% for DC-MS,
- 1.3 % for HiPIMS (B-HiPIMS_0)
- 4.2 % for bipolar HiPIMS (BHiPIMS_300)

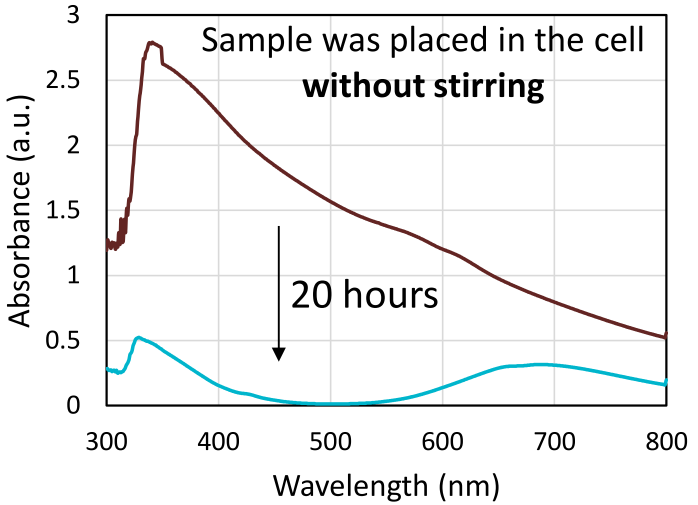
What if we sputter Copper onto castor oil ?

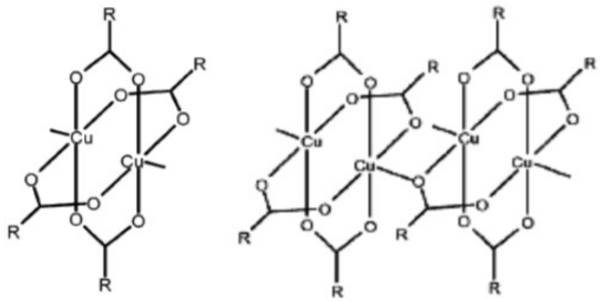
Oxidation of Cu-NPs in castor oil





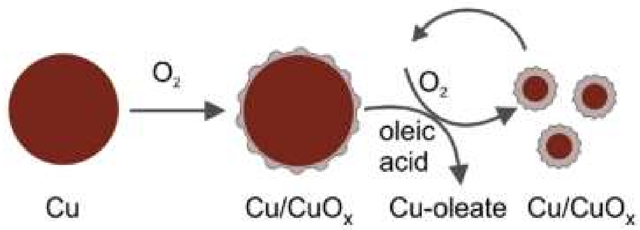






Copper (II) oleate ⟶ Cu_2O NPs

Ganguly, M. *et al. Dalt. Trans.* **43**, 11624–11636 (2014).



Nguyen, M. T. *et al. ACS Sustain. Chem. Eng.* **8**, 18167–18176 (2020).

Conclusions

1. **HiPIMS promotes the formation of bigger NPs**
   → Substitute to post-synthesis heating of the liquid [1]
   - Other parameters don't play a significant role
   - Au-NP size typically varies from ~2 (DC-MS) to 5 nm (HiPIMS)
   - Same observation was made for Ag-NP [2]
   - Increased heating rate of the liquid and/or high kin. energy of metallic species might be the reason
2. **Viscosity changes the way the NP grow**
   - Too high viscosity promotes the formation of a film, which dissolves partially afterward.
3. **The nature of the sputtered material/host liquid influences the stability of the NP solutions (see also [3])**
4. **After deposition,**
   - For Gold, secondary growth. Solution is very stable.
   - For Silver, aggregation because of the lower stability
   - Oxidation happens for Copper.

[1] B. Ingham et al, Chem. Mater. 23, 3312 (2011).
[2] A. Sergievskaya et al, *Coll. Surf. A Physicochem. Eng. Asp*. 615, 126286 (2021).
[3] X. Carette et al, *J. Phys. Chem. C* 122, 26605 (2018).