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Magnetron sputtering of copper, silver, and gold onto oils for nanoparticle synthesis.

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Advantages of sputtering onto liquids for NP synthesis

1. **Flexibility**

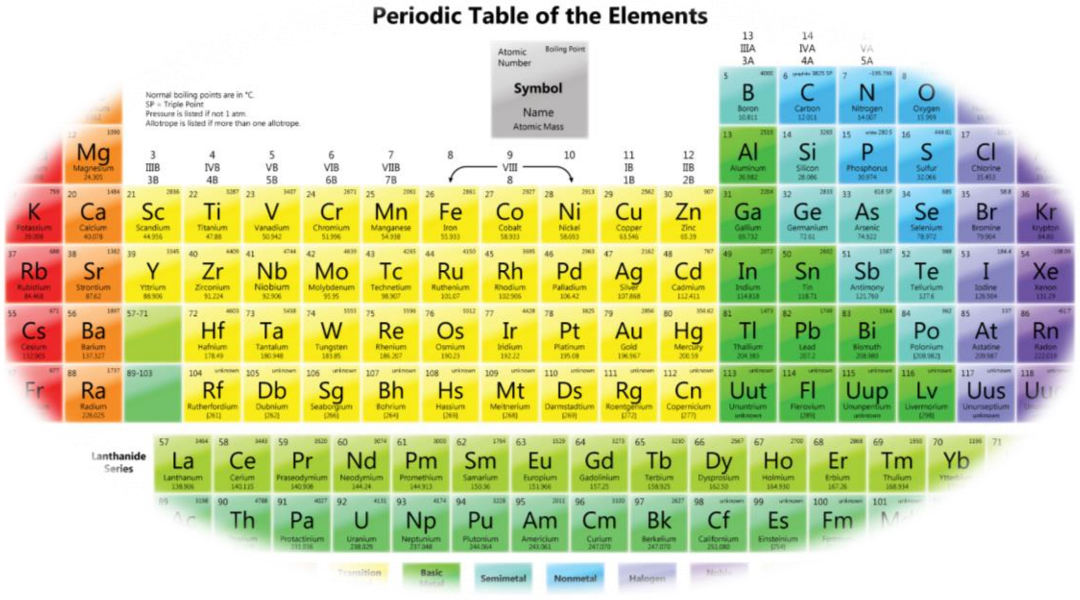
   Large variety of elements can be sputtered

2. **Reproducibility**

   “Automatized” process + controlled environment

3. **Purity**

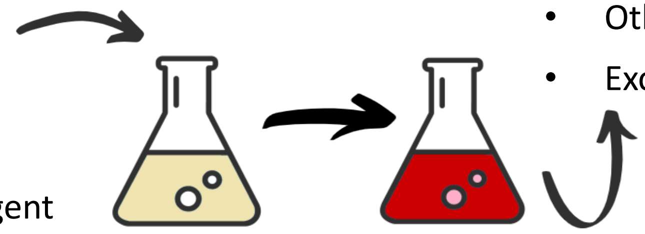
   Chemical reactants and by-products are avoided



+ O_2 / N_2 / …

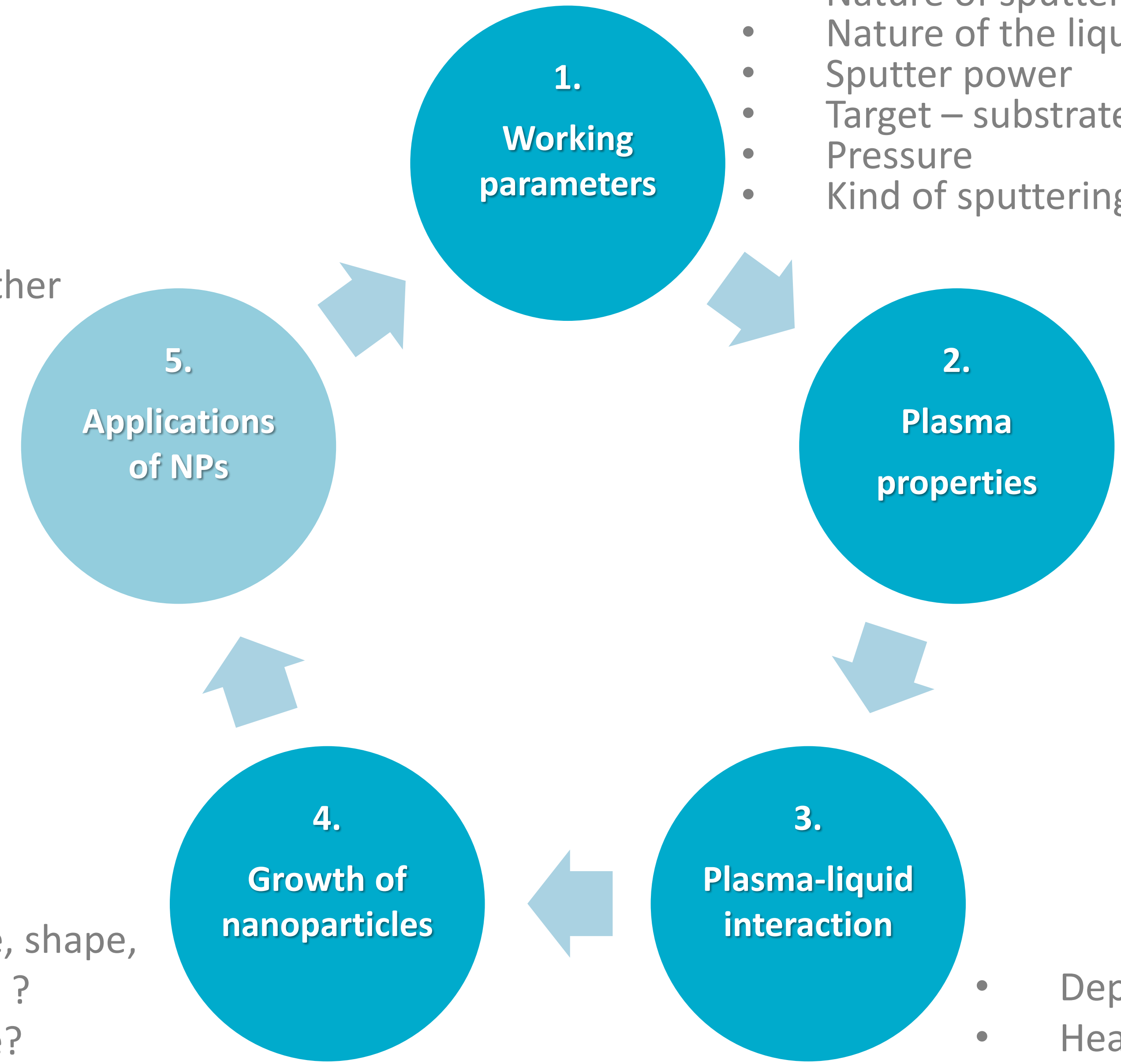
Classic colloidal synthesis

- Solvent
- Metal salt
- Reducer
- Capping agent



- Nanoparticles
- Other reaction products
- Excess of reagents

Our goal



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

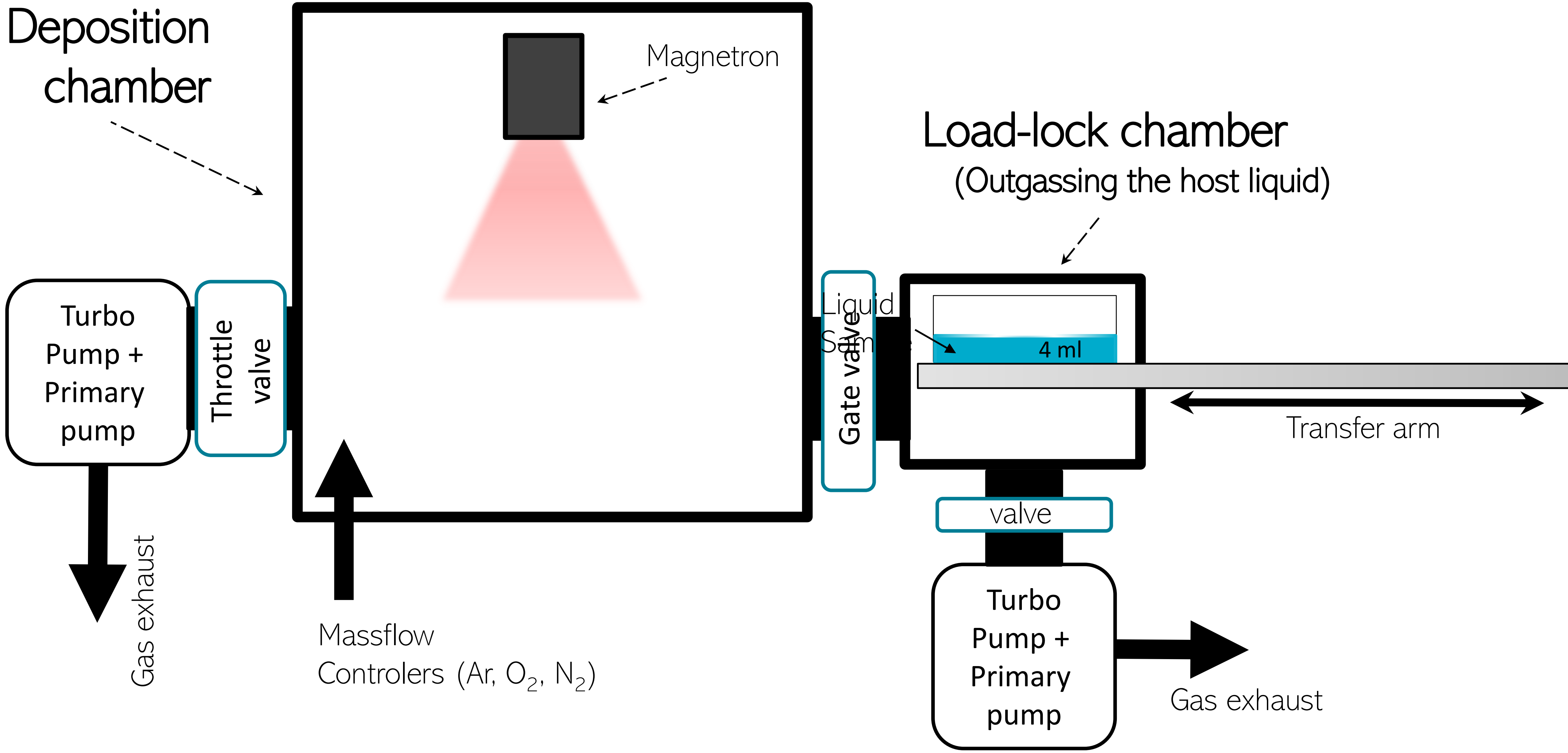
- Particle fluxes
- Kinetic energies

- Deposition rates
- Heating of the liquid
- Liquid chemistry

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

- Collaborations with other research groups

Experimental set-up

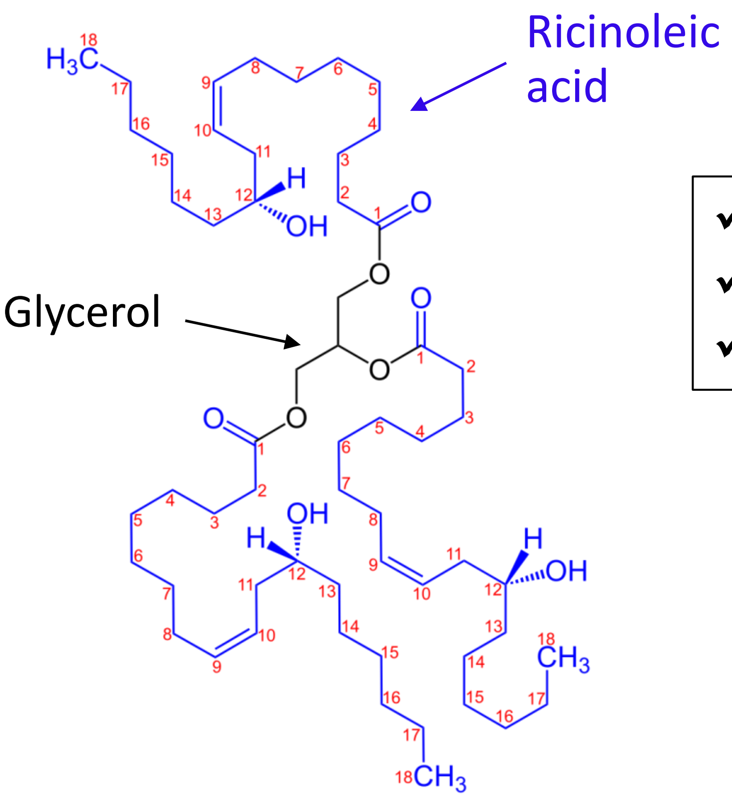


Castor oil as a host liquid

Ricinus communis

Castor beans

Ricinoleate

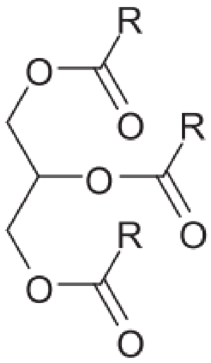


- ✓ Withstand vacuum
- ✓ Low toxicity
- ✓ Low cost

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

Methods of NP characterization:

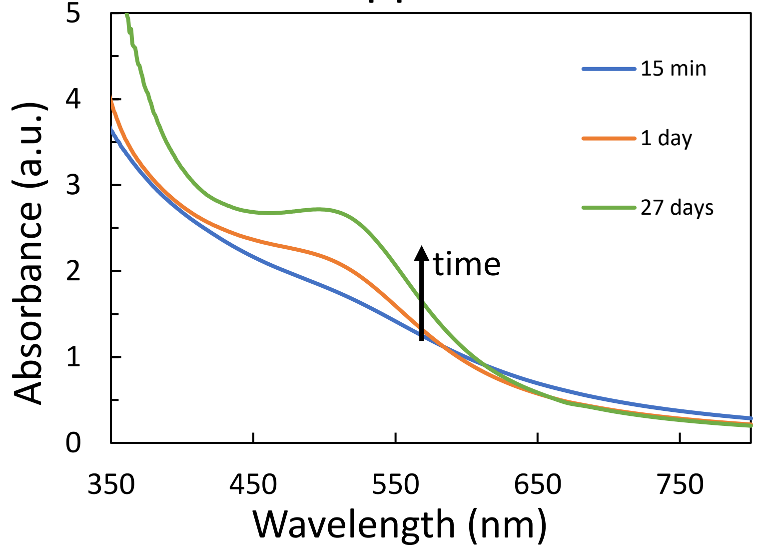
1. UV-vis spectroscopy: optical properties, colloidal stability, and ageing of NP solutions
2. TEM: size and size distribution of NPs

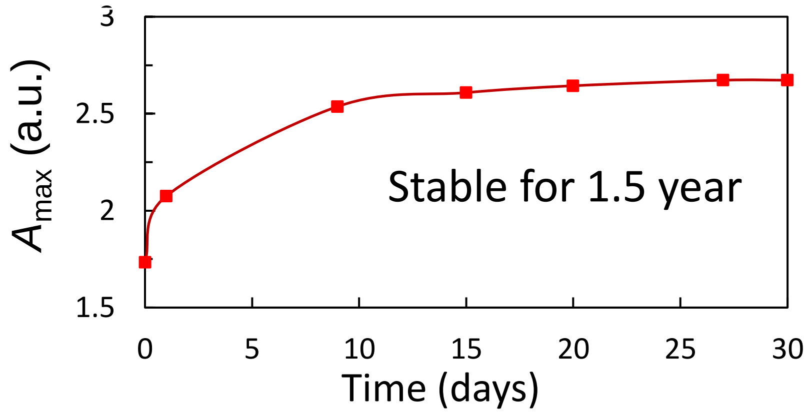
1. Sputtering Gold on Castor oil

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

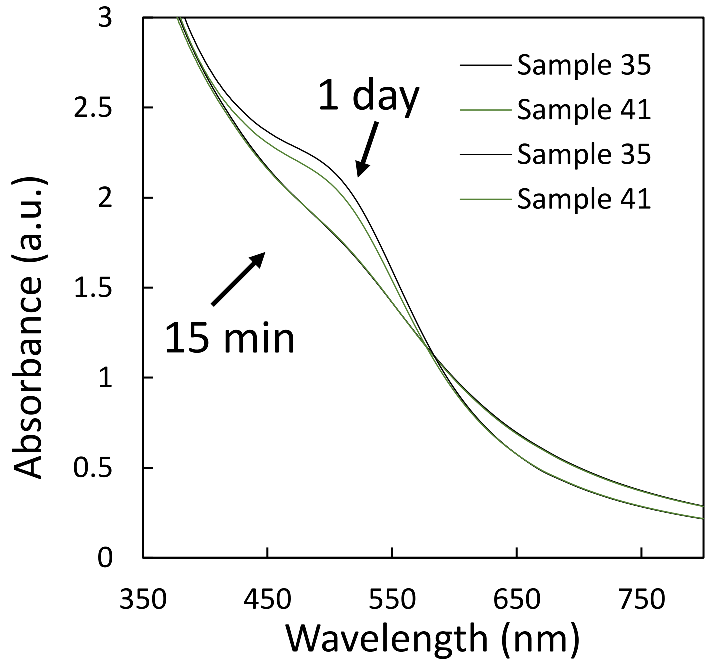
p_{Ar} = 0.5 mTorr, WD = 20 cm, t_s=5 min, P = 80 W → Flux of metal atoms : Φ = (2.5 ± 0.5)·10^{-7} mol·cm^{-2}·min^{-1}

SPR band appears with time

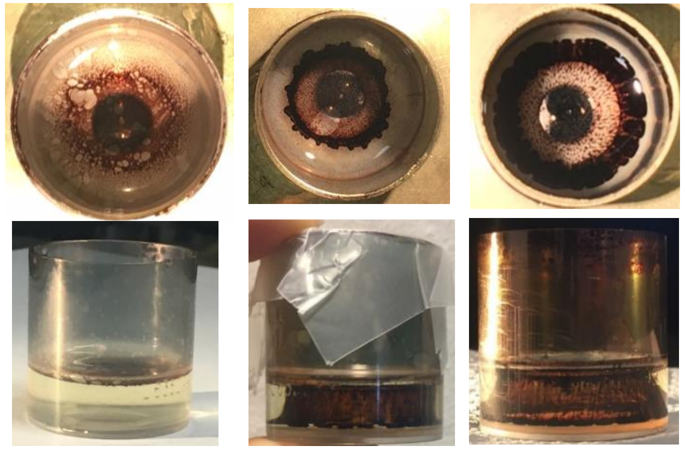




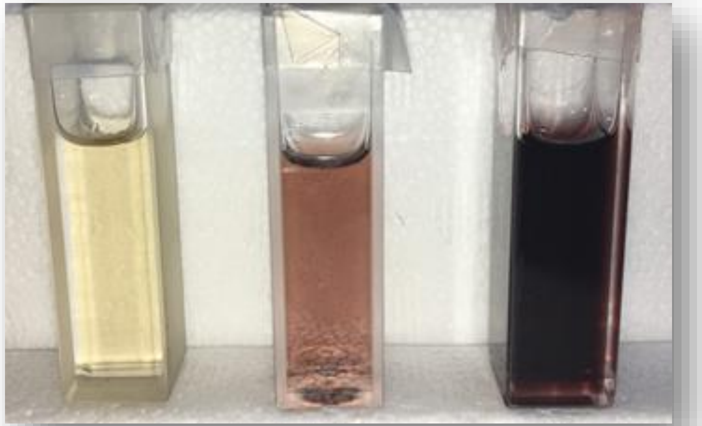
- NP continue to grow for a few days after sputtering
- NP solutions are stable for a very long time
- Good reproducibility



Effect of sputter time

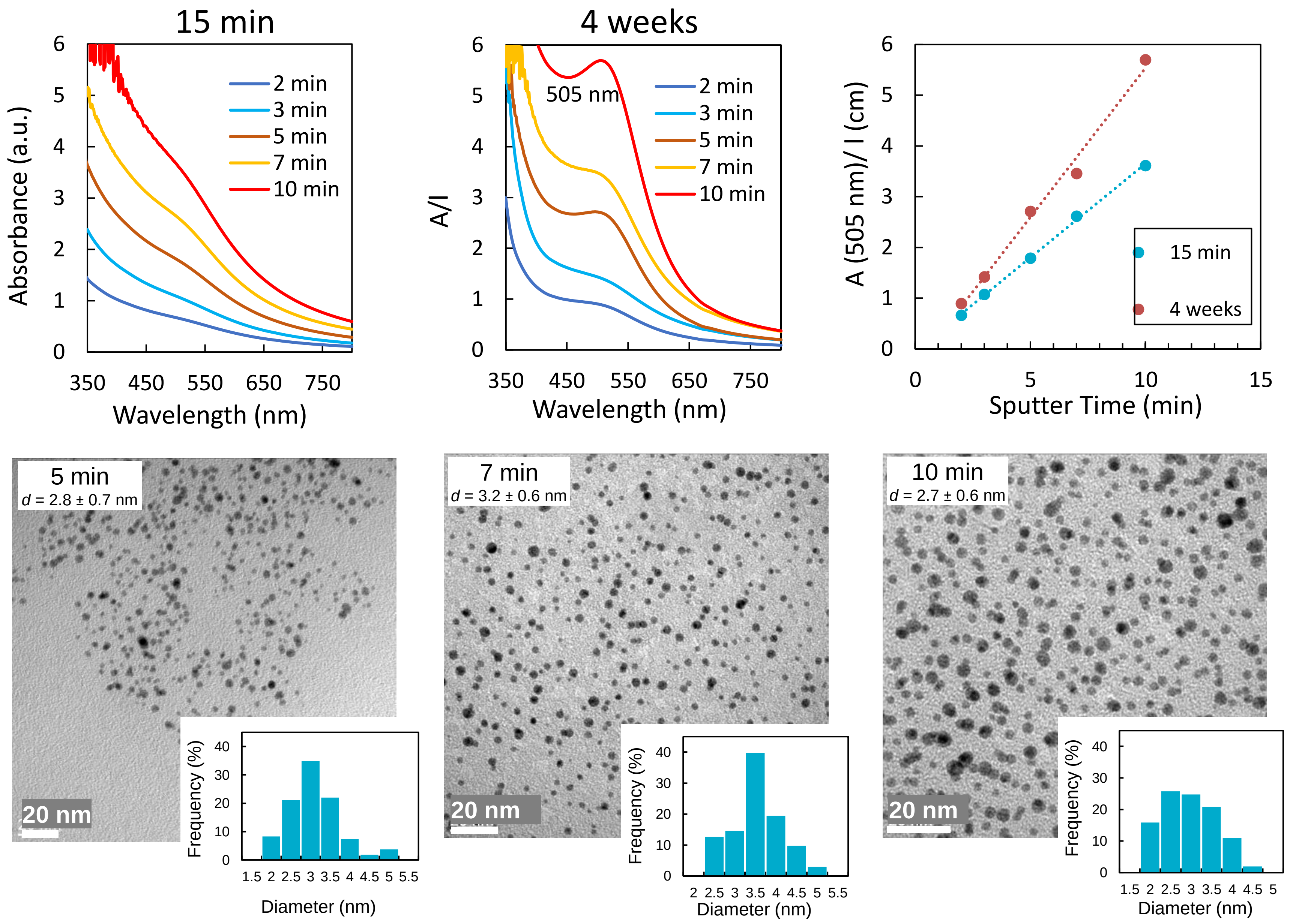


2 min 5 min 10 min

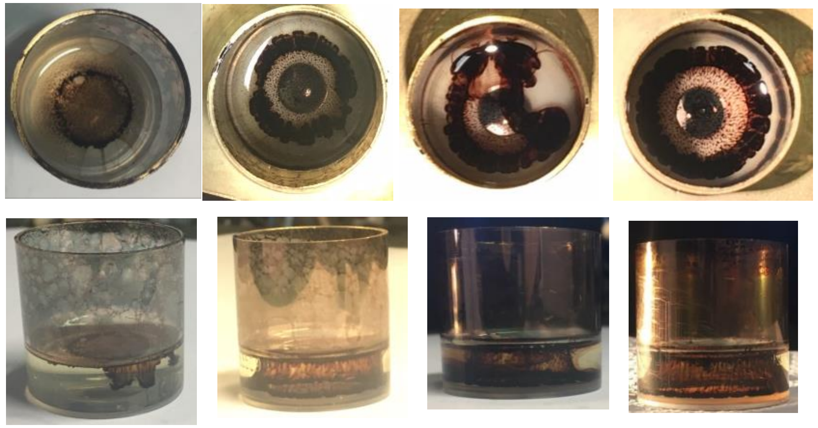


$p_{Ar} = 0.5$ mTorr, WD = 20 cm, $P = 80$ W, → Flux of metal atoms : $\Phi = (2.5 \pm 0.5)\cdot10^{-7}$ mol·cm^{-2}·min^{-1}

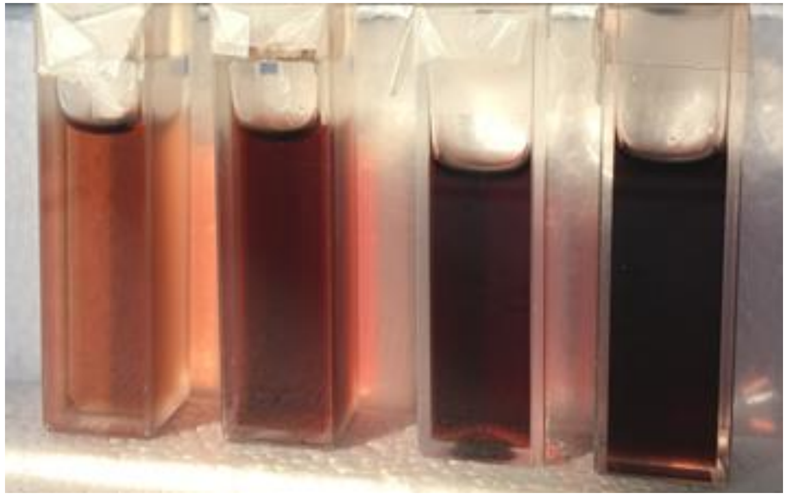
Different deposition times: ageing of the NP solutions



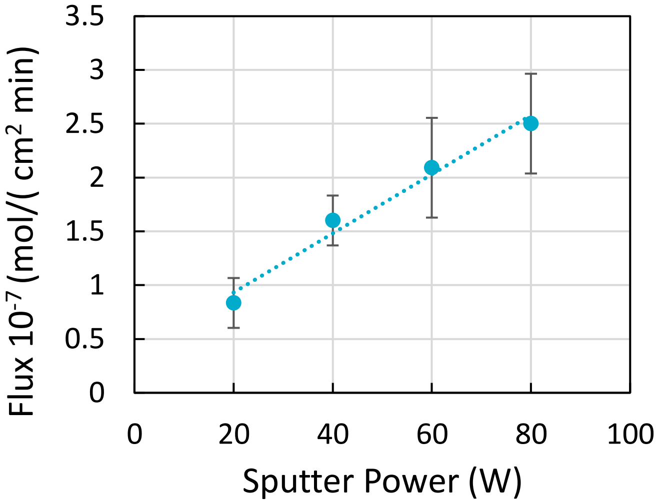
Effect of sputter power



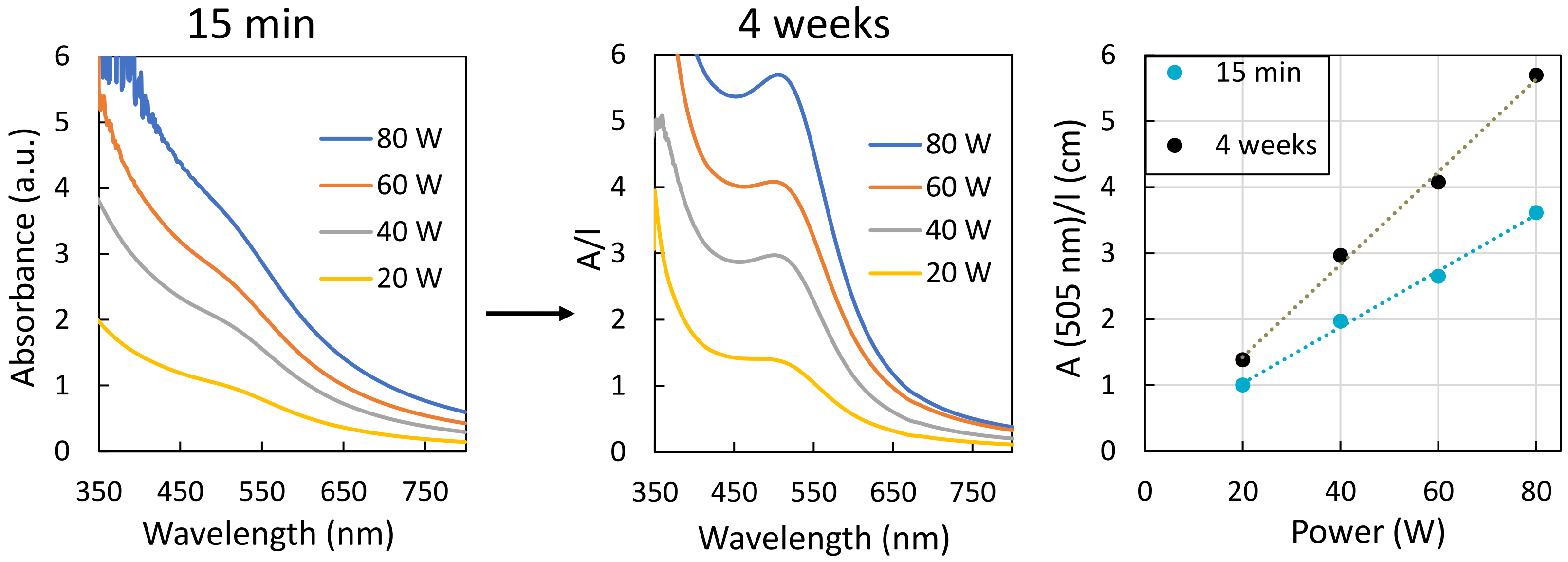
20 W 40W 60W 80W

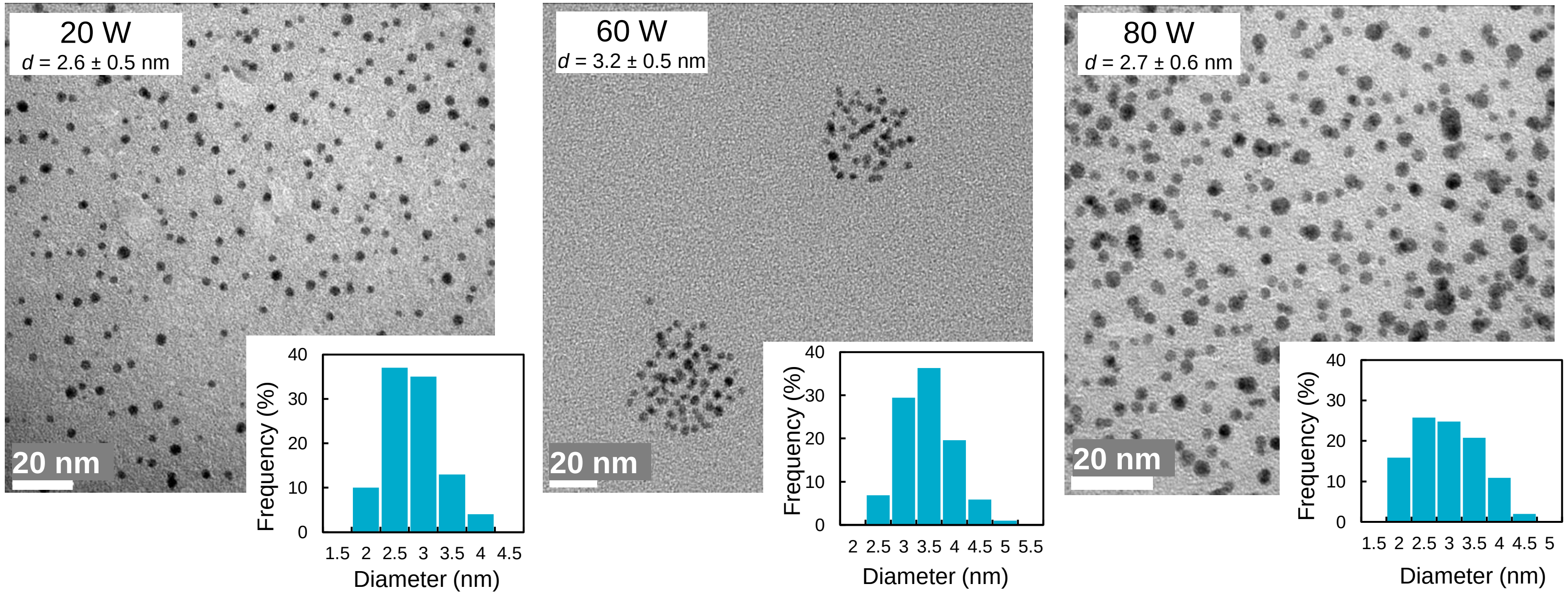


p_{Ar} = 0.5 mTorr, WD = 20 cm, t_s = 10 min



Different sputter powers : ageing of the NP solutions





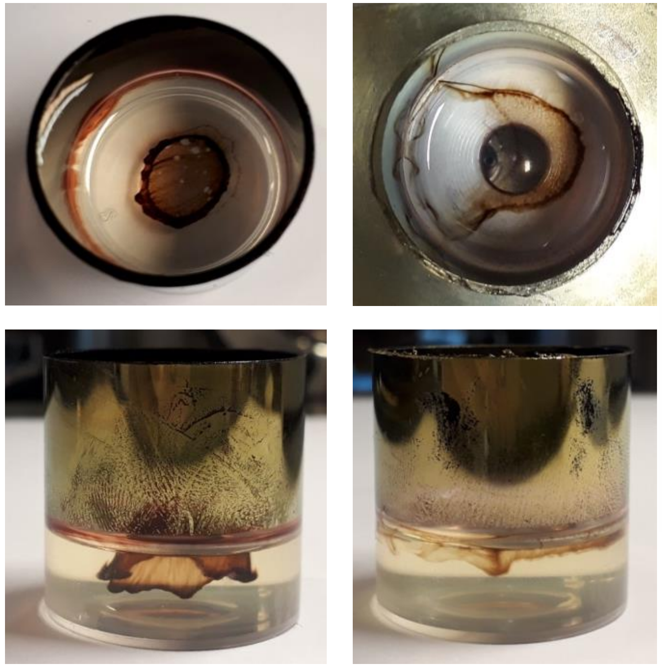
DC-MS *vs.* (unipolar) HiPIMS

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

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

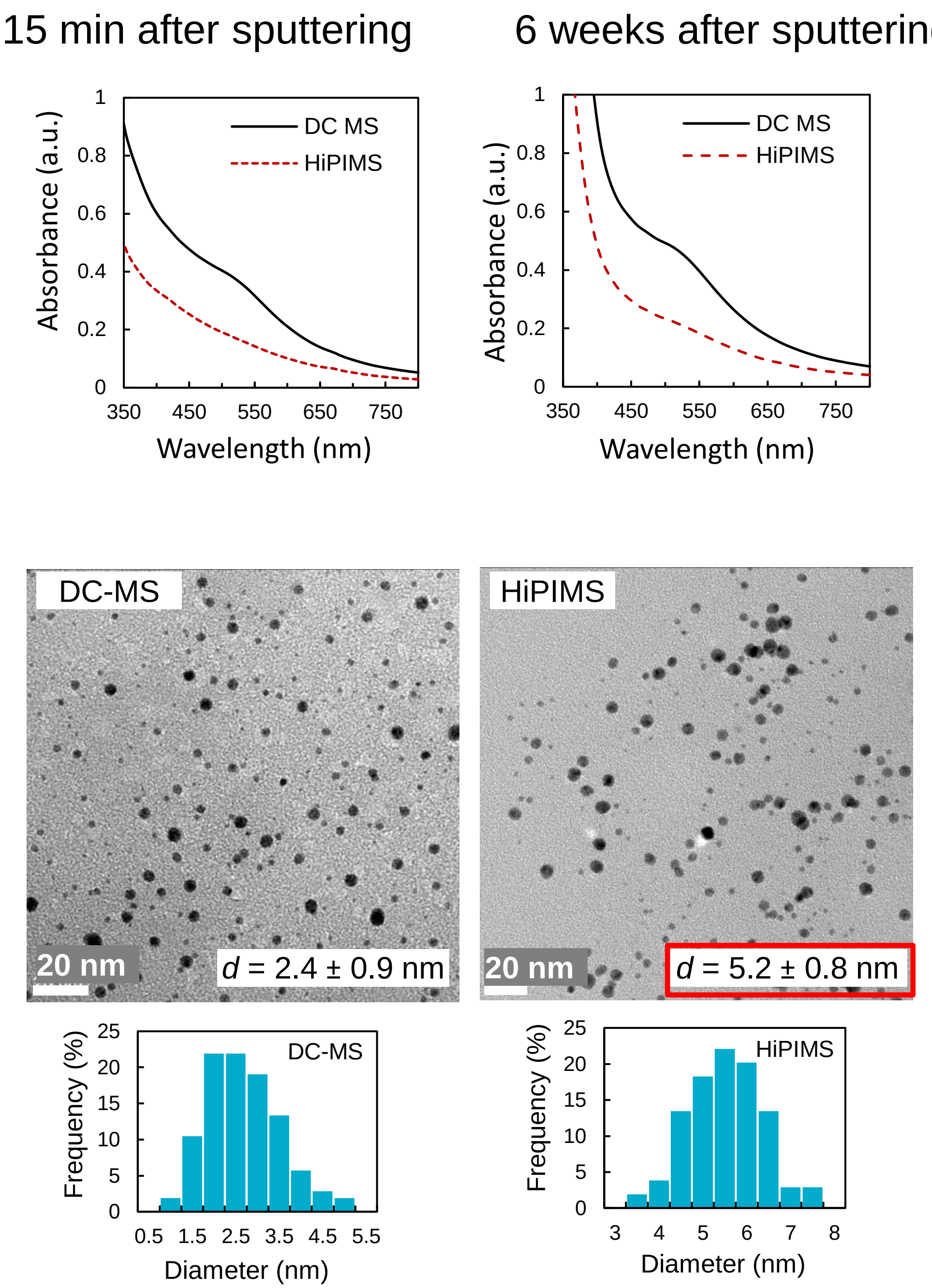
HiPIMS:
T_{on} = 20 µs, I_{pk} = 0.3 A/cm^2, f = 800 Hz,
$\Phi = (0.9 \pm 0.1) \cdot 10^{-7}$ moles/cm^2 min

DC-MS HiPIMS



DC-MS HiPIMS

Ageing of the NP solutions

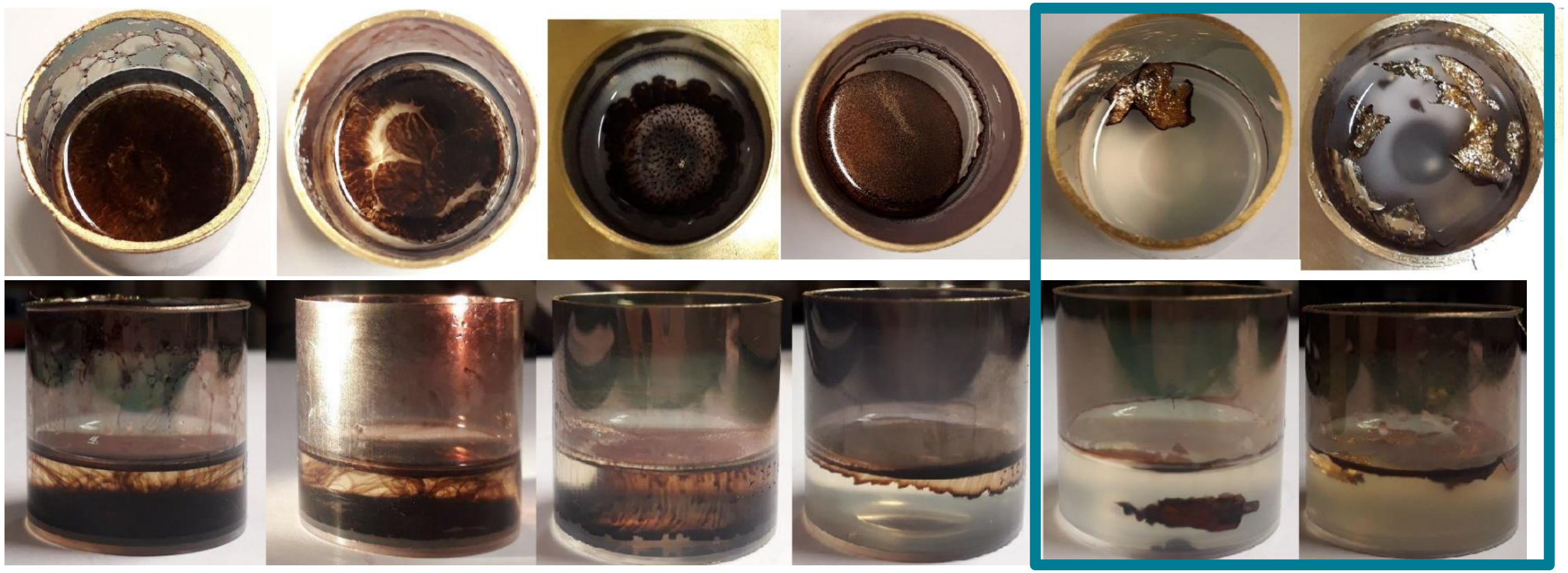


Effect of the liquid viscosity

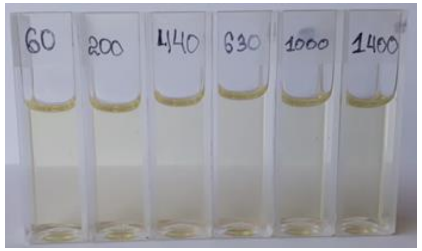
0.5 mTorr, 20 cm, 80 W, 10 min, Liquid : **polymerized* rapeseed oil**

* Plasma treatment prior sputtering

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



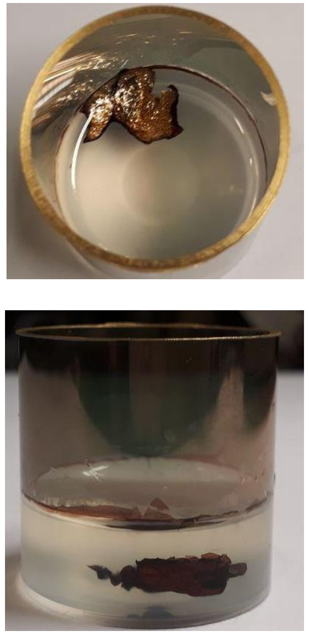
Surface tension
~ 32.7 mJ · m^{-2}



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

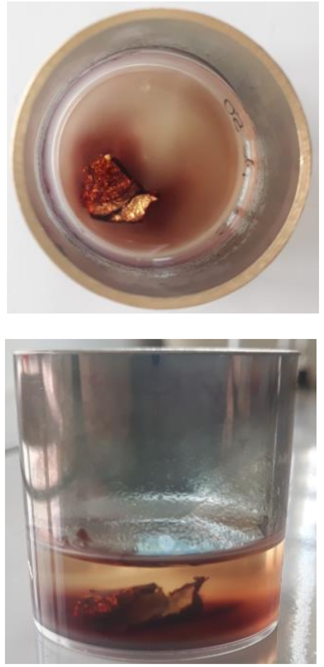
Film is obtained
like on a solid surface

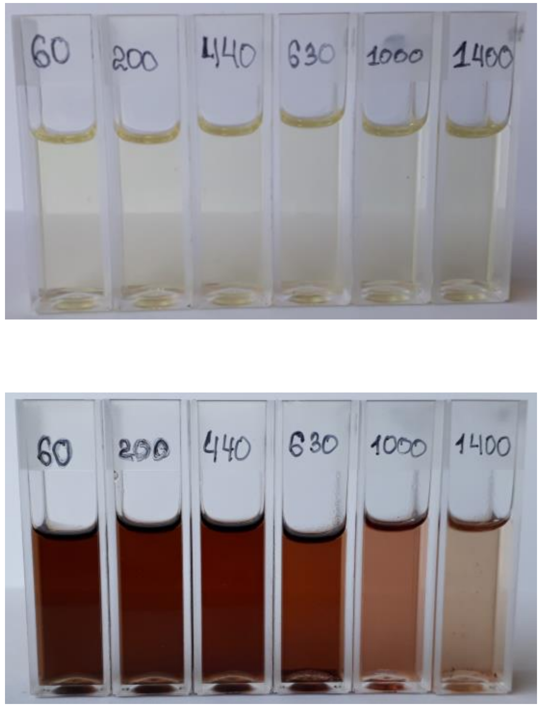
Effect of the liquid viscosity

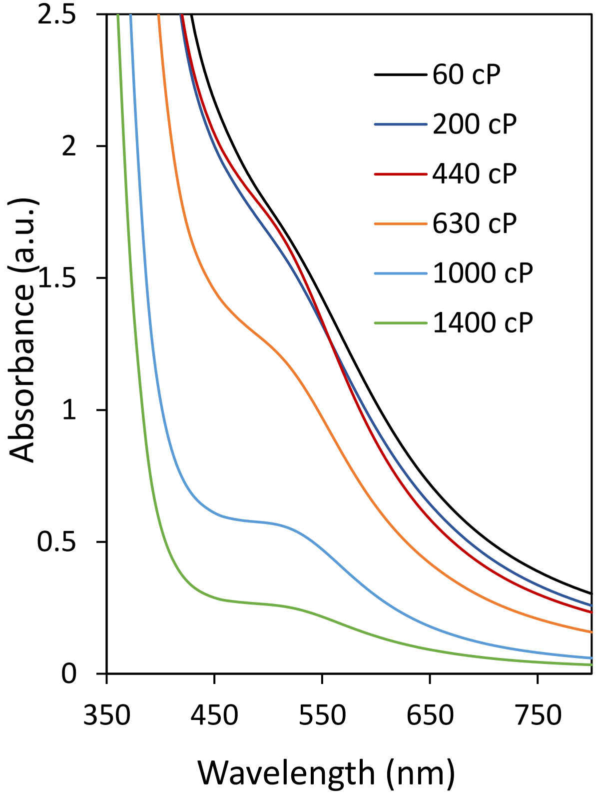


5 months

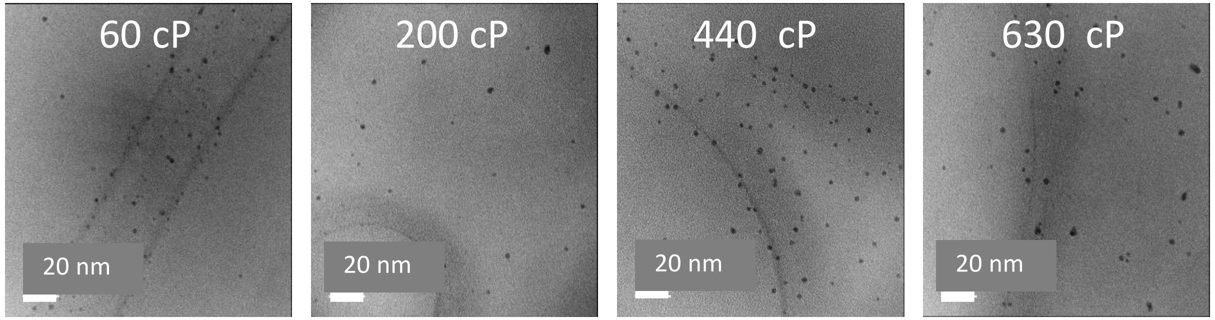
Migration
of NPs in solution



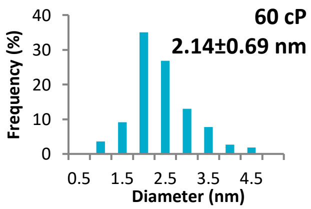


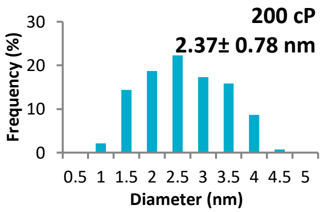


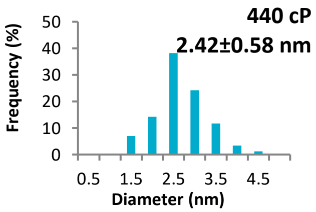
Effect of the host liquid viscosity

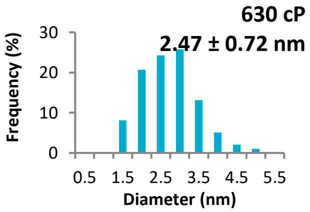


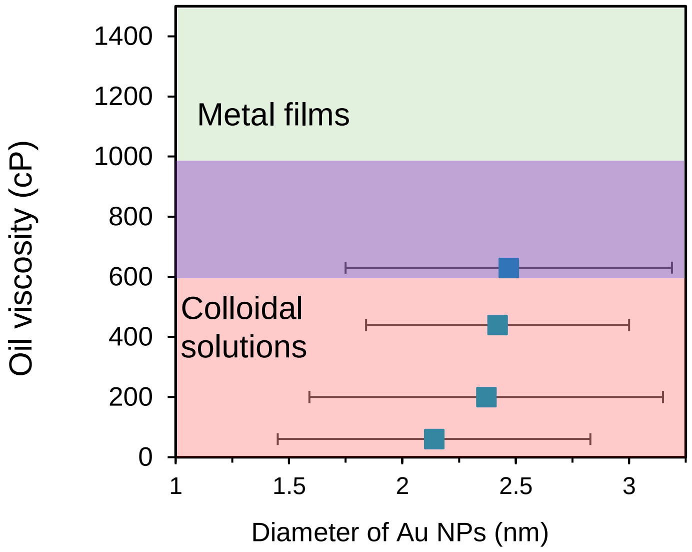
No TEM data for high viscosity liquids: impossible to remove
 the liquid from the TEM grid
XRD data for Au films
d_{Au} (1000 cP) = (10 ± 1) nm
d_{Au} (1400 cP) = (13 ± 2) nm









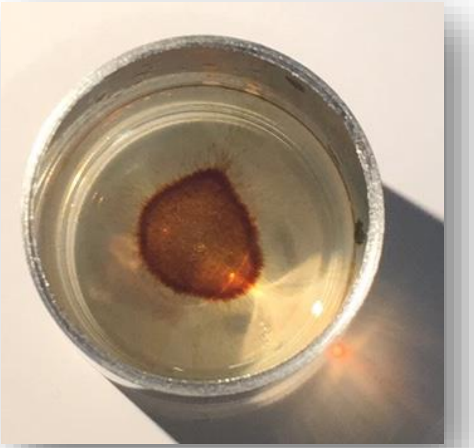


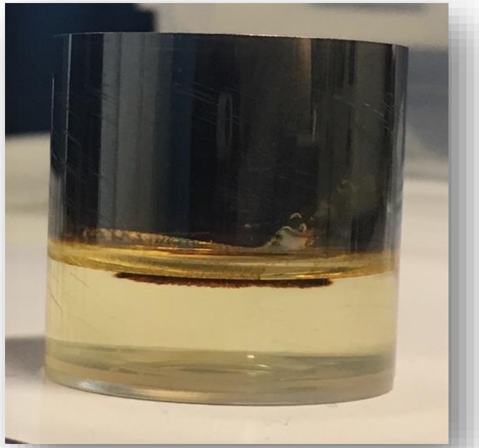
2. What if we sputter silver onto castor oil ?

DC-MS of silver target onto castor oil

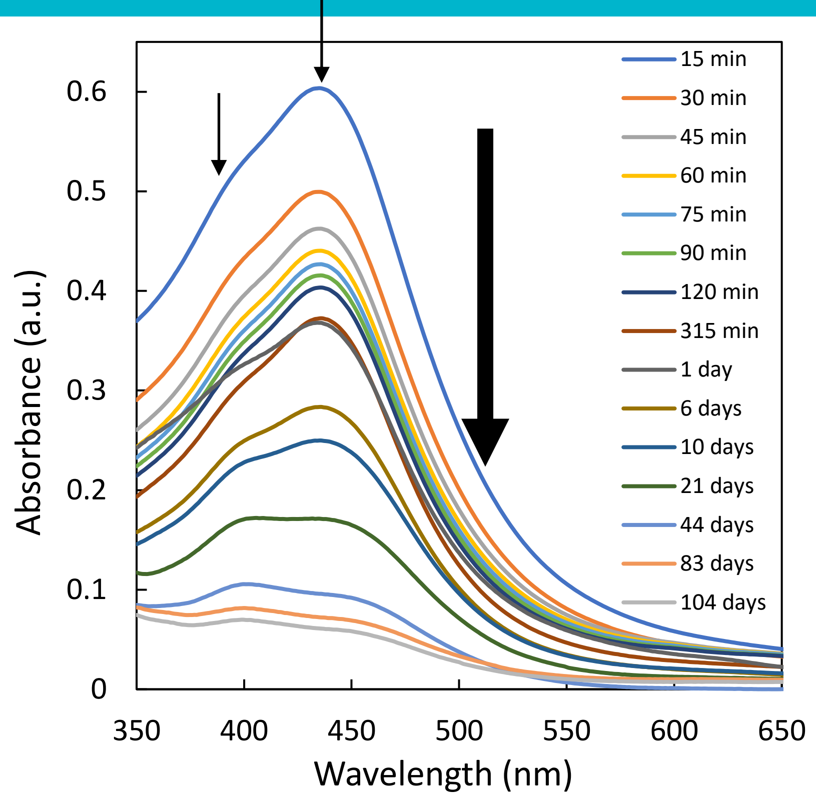
0.5 mTorr, 20 cm, 80 W, 3 min

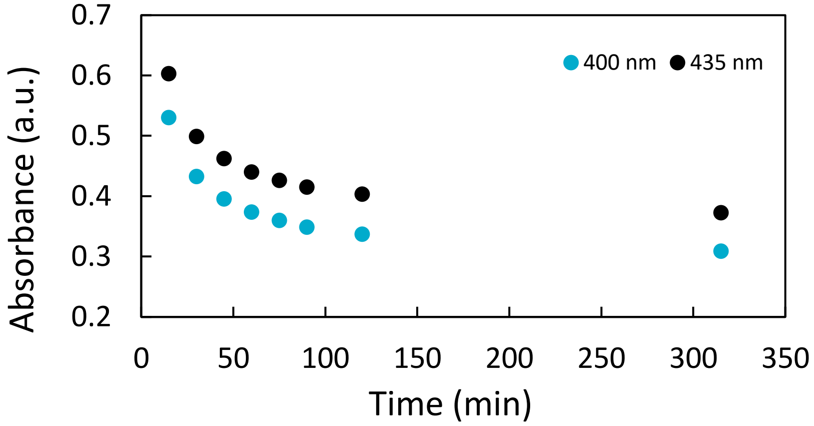
$\Phi = (0.6 \pm 0.1) \cdot 10^{-7}$ moles/cm$^2\cdot$min

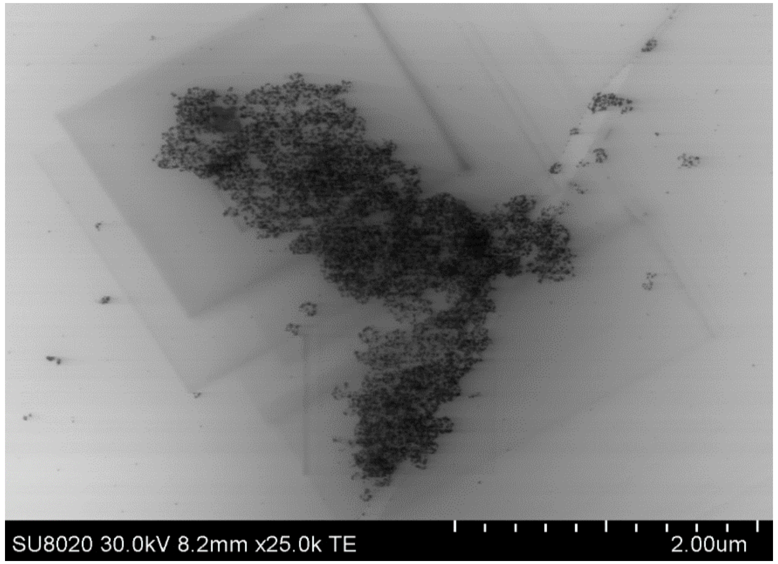


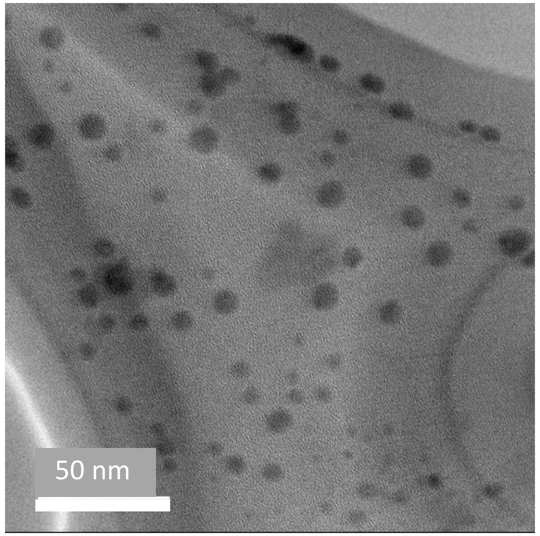


Ageing of the Ag-NP solutions







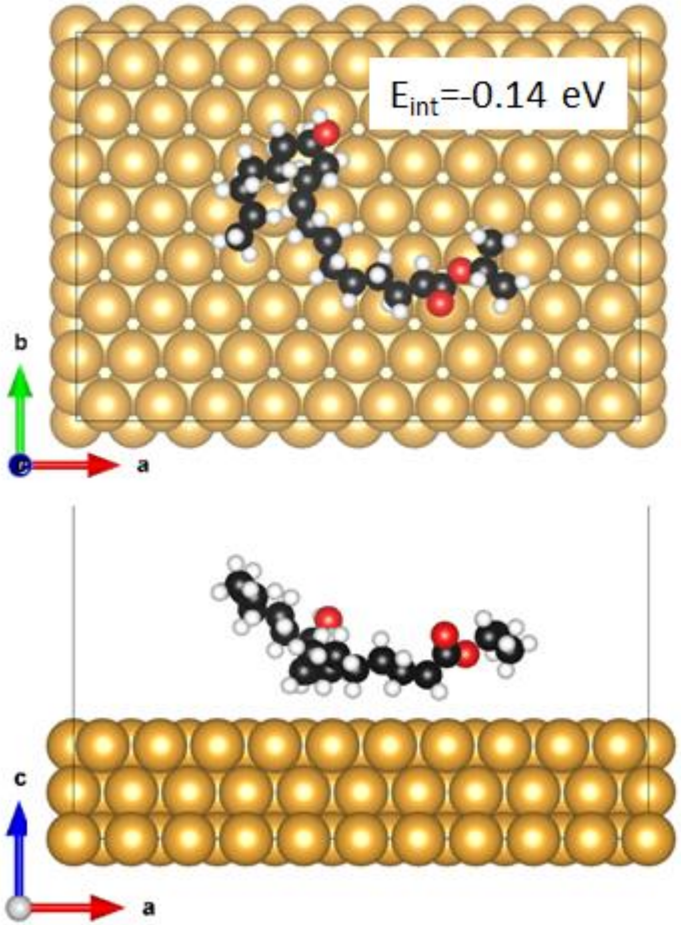


8.1 nm ± 5.0 nm.
TEM image 8 months after preparation.

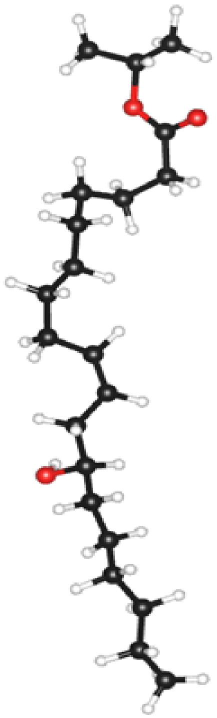
Stability of nanoparticles in castor oil: Interaction energy calculations

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

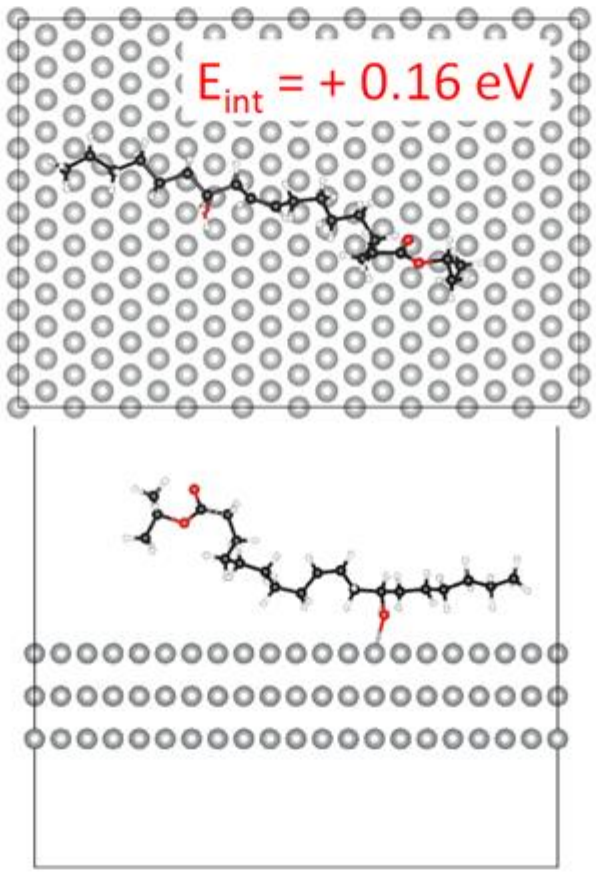
GOLD



1/3 of triglyceride of ricinoleic acid



SILVER

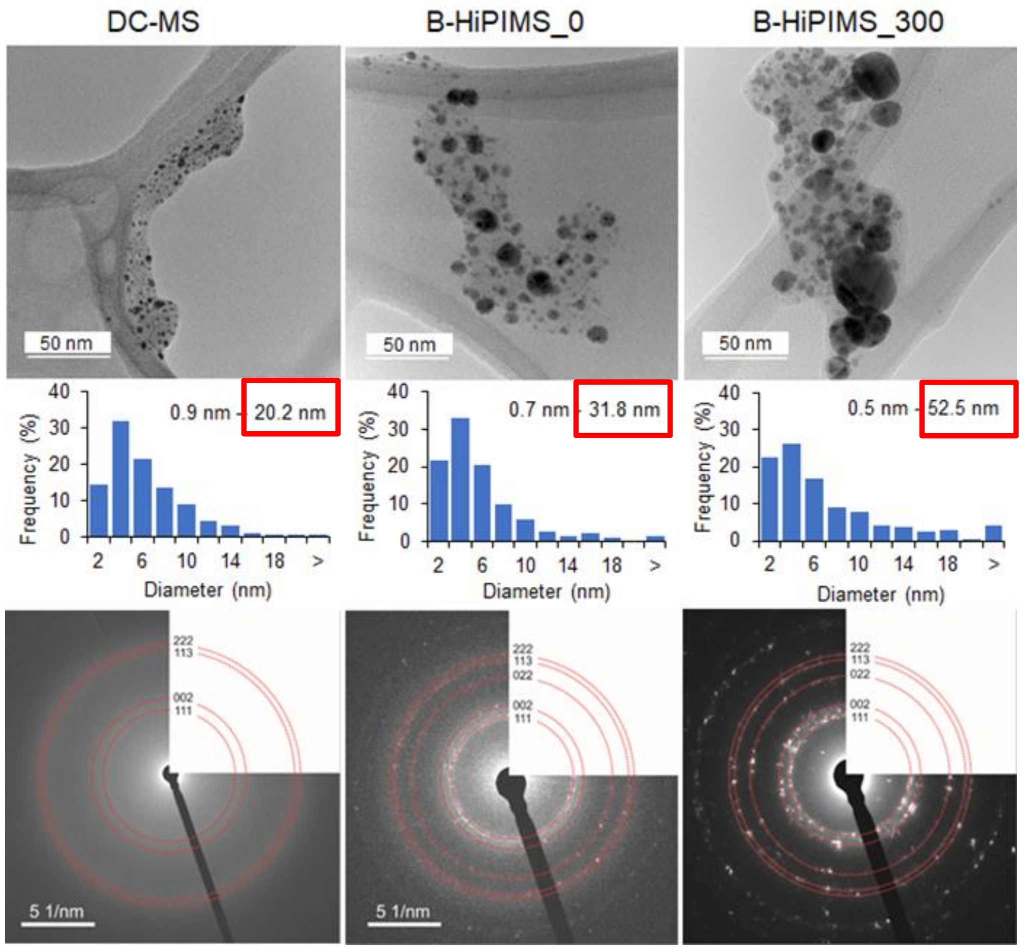


DC-MS *vs.* Unipolar & Bipolar HiPIMS

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

Flux HiPIMS: (0.9 ± 0.1)·10^{-7} moles/cm^2 min
f = 800 Hz, $T_{ON,-}$ = 20 µs, I_{pk} = 0.3 A/cm^2

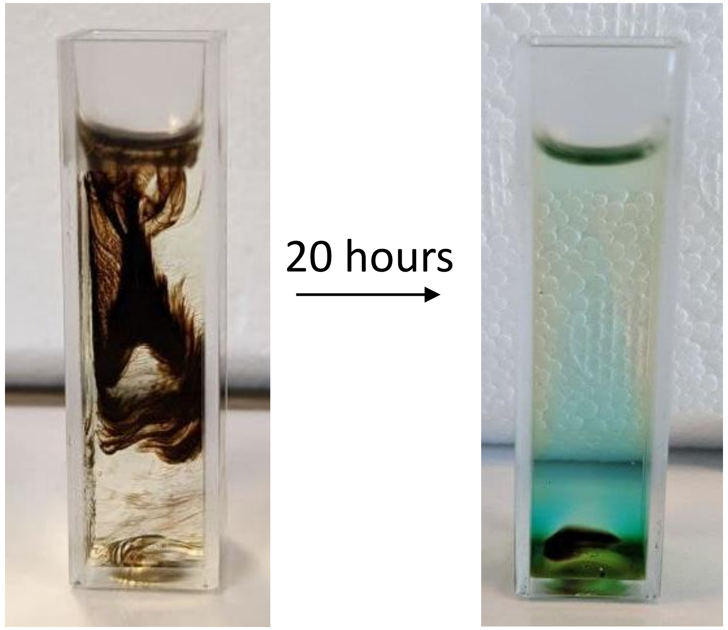
Flux B-HiPIMS: (0.2 ± 0.1)·10^{-7} moles/cm^2 min
f = 800 Hz, $T_{ON,-}$ = 20 µs, I_{pk} = 0.3 A/cm^2
V_+ = +300V, $T_{ON,+}$ = 250 µs, $T_{+/-}$ = 10µs

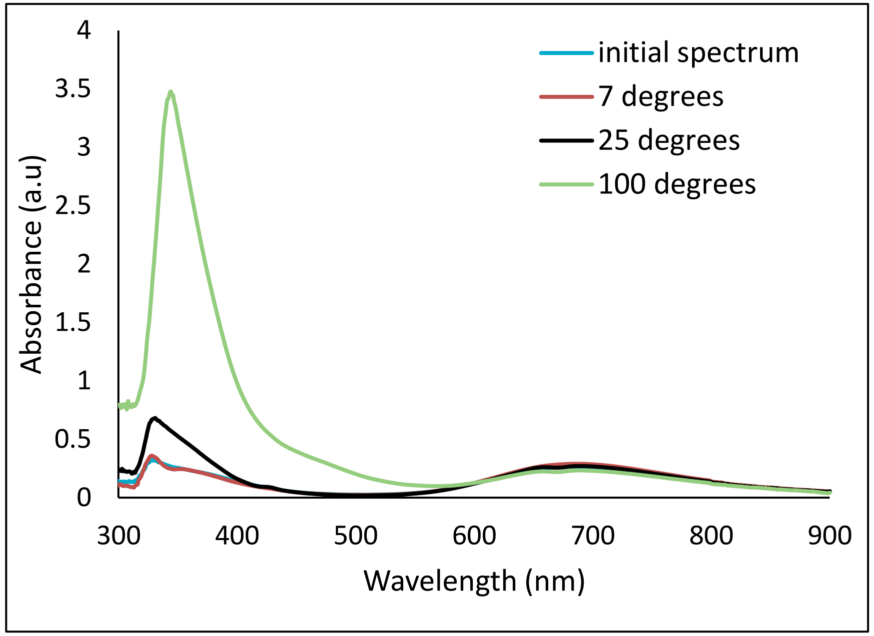


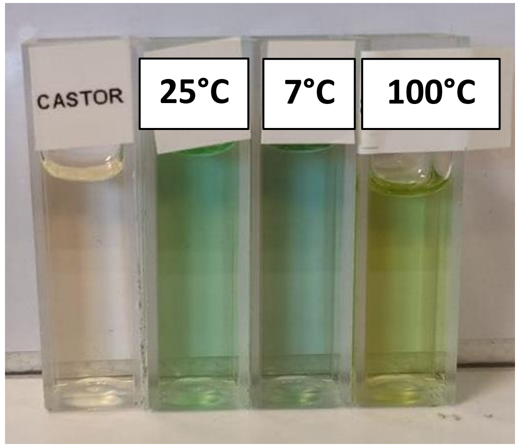
Number of particles larger than 20 nm
- 0.1% for DC-MS,
- 1.3 % for HiPIMS (B-HiPIMS_0)
- 4.2 % for bipolar HiPIMS (BHiPIMS_300)

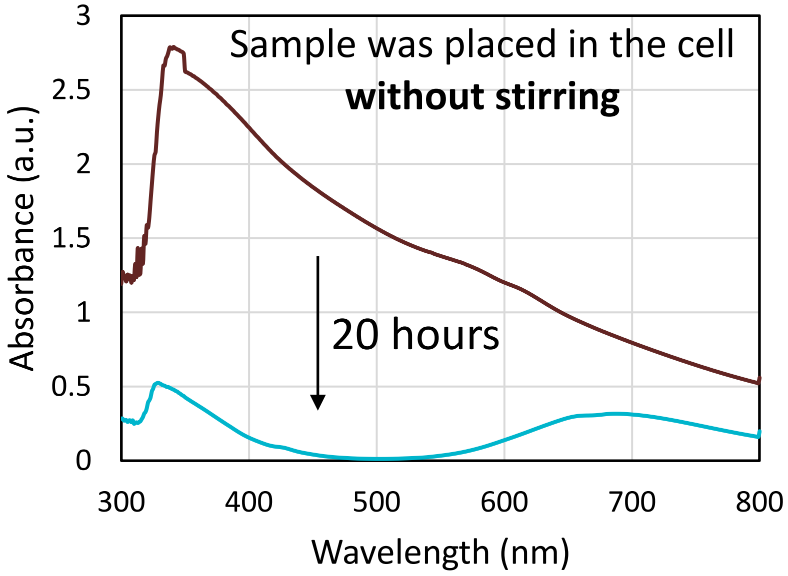
3. What if we sputter copper onto castor oil ?

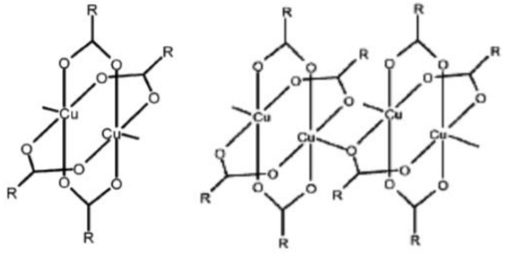
Oxidation of Cu-NPs in castor oil





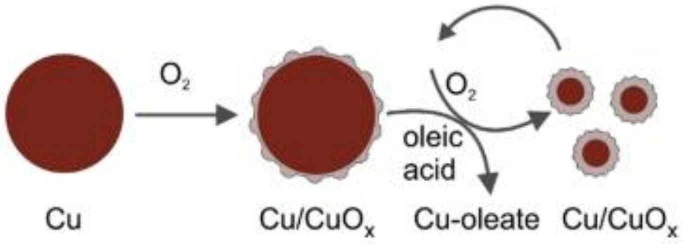






Copper (II) oleate ⟶ Cu_2O NPs

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



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

Sputtering onto Liquids: mechanism of NP formation