

SPUTTERING ONTO LIQUIDS FOR NANOPARTICLE SYNTHESIS

Stephanos KONSTANTINIDIS¹, Amy O'REILLY¹, Kamakshi PATEL¹, Adrien CHAUVIN¹, Julien DE WINTER¹,
David CORNIL¹, Jérôme CORNIL¹, Adriano PANEPINTO², Jozef VESELÝ³, Halima ALEM-MARCHAND⁴,
Anastasiya SERGIEVSKAYA¹

¹ University of Mons - Mons (BELGIUM)

² Materia Nova - Mons (BELGIUM)

³ Charles University - Prague (CZECH REPUBLIC)

⁴ Institut Jean Lamour - Nancy (FRANCE)

stephanos.konstantinidis@umons.ac.be

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

Periodic Table of the Elements

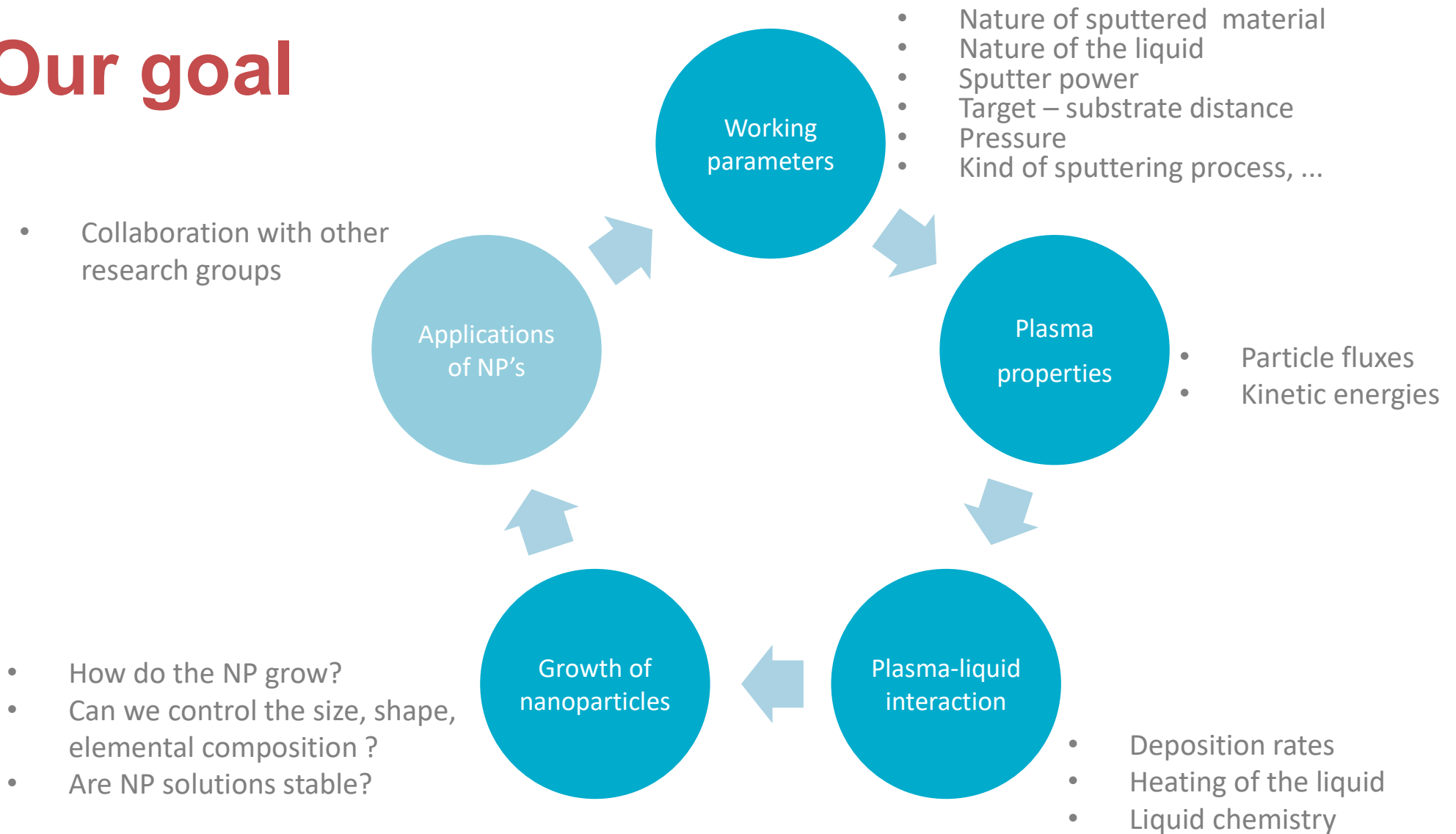
Normal boiling points are in °C.
BP = Triple Point
Pressure is fixed at not 1 atm.
Abbreviations in bold if more than one allotope.

Atomic Number	Symbol	Name	Atomic Mass
1	H	Hydrogen	1.00794
2	He	Helium	4.002602
3	Li	Lithium	6.941
4	Be	Beryllium	9.012182
5	B	Boron	10.811
6	C	Carbon	12.0107
7	N	Nitrogen	14.006434
8	O	Oxygen	15.999
9	F	Fluorine	18.9984032
10	Ne	Neon	20.1797
11	Na	Sodium	22.98976928
12	Mg	Magnesium	24.304
13	Al	Aluminum	26.9815386
14	Si	Silicon	28.0855
15	P	Phosphorus	30.973762
16	S	Sulfur	32.06
17	Cl	Chlorine	35.45
18	Ar	Argon	39.948
19	K	Potassium	39.0983
20	Ca	Calcium	40.078
21	Sc	Scandium	44.955912
22	Ti	Titanium	47.88
23	V	Vanadium	50.9415
24	Cr	Chromium	51.9961
25	Mn	Manganese	54.938045
26	Fe	Iron	55.845
27	Co	Cobalt	58.933195
28	Ni	Nickel	58.6934
29	Cu	Copper	63.546
30	Zn	Zinc	65.38
31	Ga	Gallium	69.723
32	Ge	Germanium	72.630
33	As	Arsenic	74.9216
34	Se	Selenium	78.96
35	Br	Bromine	79.904
36	Kr	Krypton	83.80
37	Rb	Rubidium	85.4678
38	Sr	Strontium	87.62
39	Y	Yttrium	88.90584
40	Zr	Zirconium	91.224
41	Nb	Niobium	92.90638
42	Mo	Molybdenum	95.94
43	Tc	Technetium	98.9062
44	Ru	Ruthenium	101.07
45	Rh	Rhodium	102.9055
46	Pd	Palladium	106.3635
47	Ag	Silver	107.8682
48	Cd	Cadmium	112.411
49	In	Indium	114.818
50	Sn	Tin	118.710
51	Sb	Antimony	121.757
52	Te	Tellurium	127.6
53	I	Iodine	126.905
54	Xe	Xenon	131.29
55	Cs	Cesium	132.90545
56	Ba	Barium	137.327
57	La	Lanthanum	138.90547
58	Ce	Cerium	140.12
59	Pr	Praseodymium	140.90766
60	Nd	Neodymium	144.242
61	Pm	Promethium	144.9127
62	Sm	Samarium	150.36
63	Eu	Europium	151.964
64	Gd	Gadolinium	157.25
65	Tb	Terbium	158.92532
66	Dy	Dysprosium	162.50015
67	Ho	Holmium	164.93033
68	Er	Erbium	167.259
69	Tm	Thulium	168.93032
70	Yb	Ytterbium	173.05448
71	Lu	Lutetium	174.967
72	Hf	Hafnium	178.49
73	Ta	Tantalum	180.94788
74	W	Tungsten	183.84
75	Re	Rhenium	186.207
76	Os	Osmium	190.23
77	Ir	Iridium	192.222
78	Pt	Platinum	195.084
79	Au	Gold	196.966569
80	Hg	Mercury	200.59
81	Tl	Thallium	204.3833
82	Pb	Lead	207.2
83	Bi	Bismuth	208.9804
84	Po	Polonium	209
85	At	Astatine	210
86	Rn	Radon	222
87	Fr	Francium	223
88	Ra	Radium	226
89-103	Lanthanide Series		
104	Rf	Rutherfordium	261
105	Db	Dubnium	262
106	Sg	Seaborgium	266
107	Bh	Berkelium	267
108	Hs	Hassium	277
109	Mt	Moscovium	288
110	Ds	Darmstadtium	285
111	Rg	Röntgenium	289
112	Cn	Copernicium	285
113	Uut	Ununtrium	288
114	Fl	Flerovium	289
115	Uup	Ununpentium	288
116	Lv	Livermorium	293
117	Uus	Ununseptium	294
118	Uu	Ununoctium	294

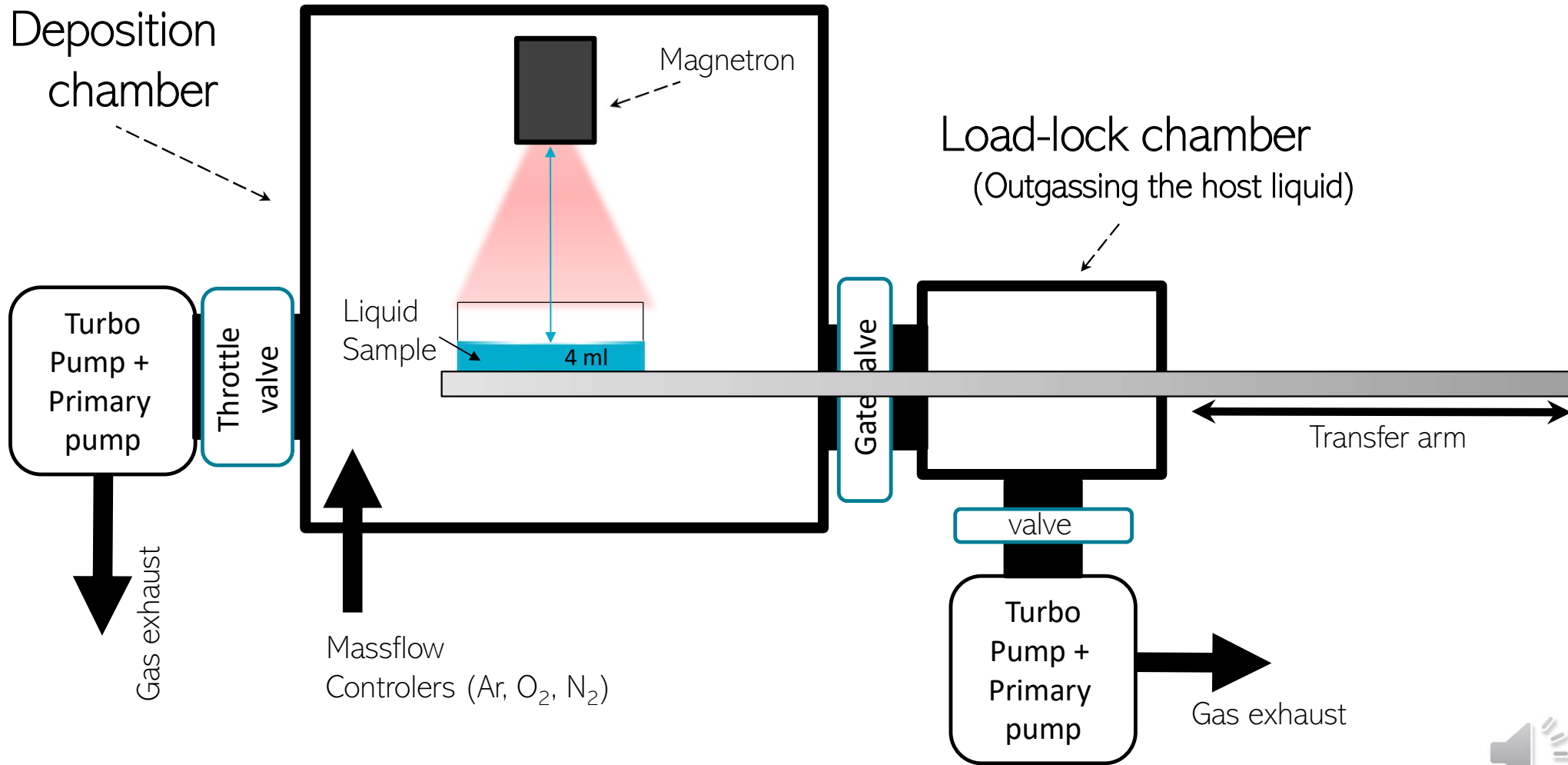
+ O₂ / N₂ / ...



Our goal



Experimental set-up



Castor oil as a host liquid



Ricinus communis

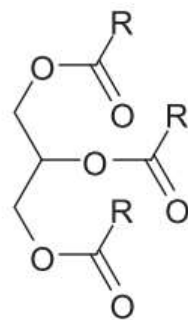
Castor beans



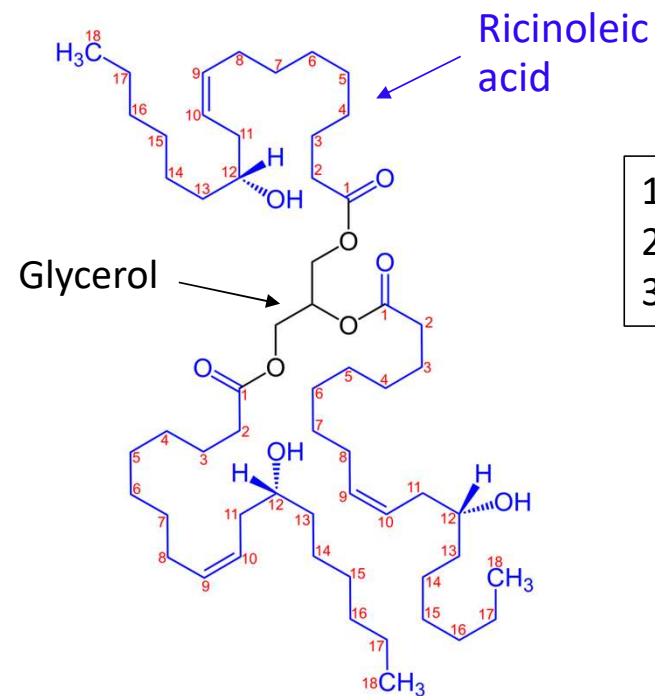
Castor oil = mixture of triglycerides

- ricinoleate ~ 90 %
- oleate ~ 7%
- linoleate ~ 3%

Generic Triglyceride



Ricinoleate



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



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)

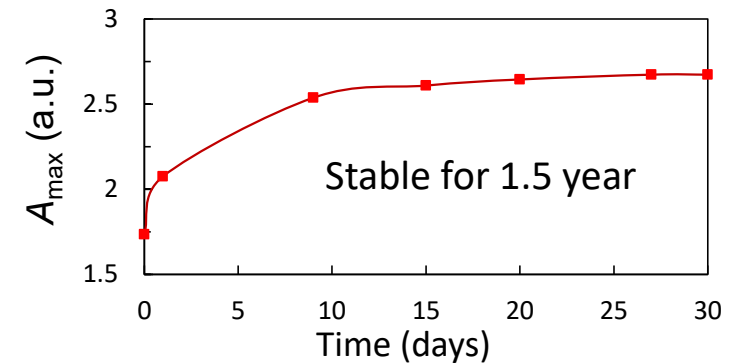
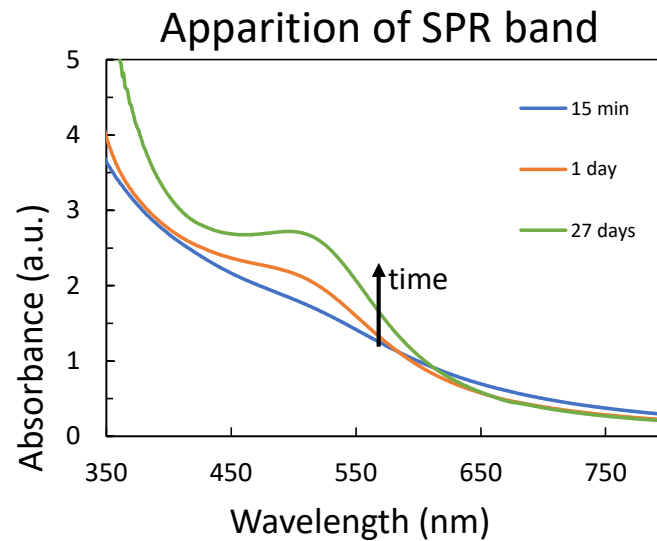
TEM and UV-Vis spec. provide info about

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



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

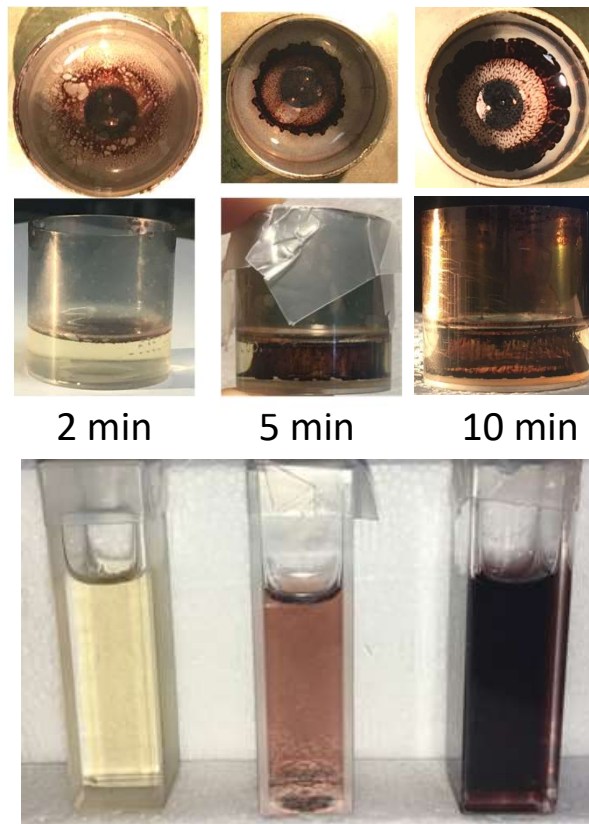
$P_{Ar} = 0.5$ mTorr, T-S dist.: 20 cm, 5 min, 80 W \rightarrow Flux of metal atoms : $\Phi = (2.5 \pm 0.5) \cdot 10^{-7}$ mol \cdot cm $^{-2}\cdot$ min $^{-1}$



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

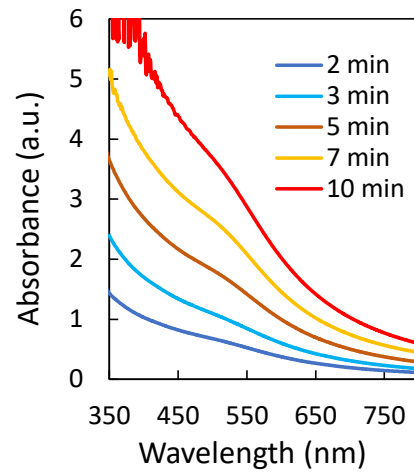


Effect of sputter time

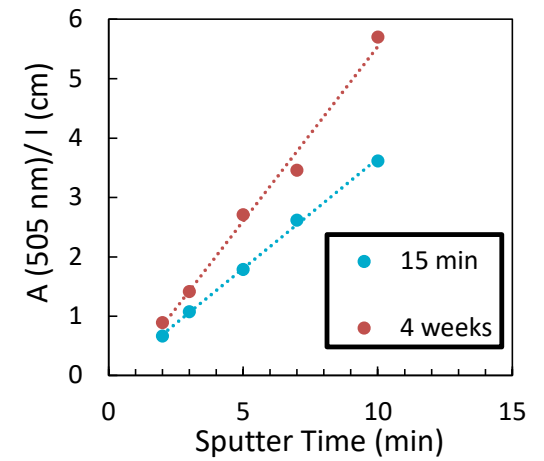
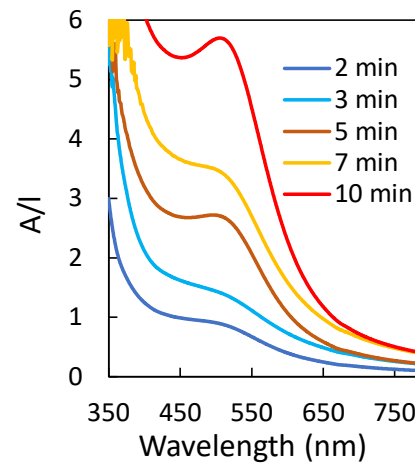


Ageing of the NP solutions

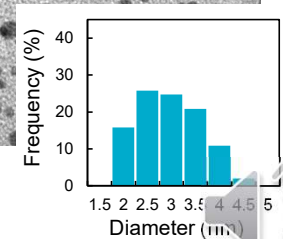
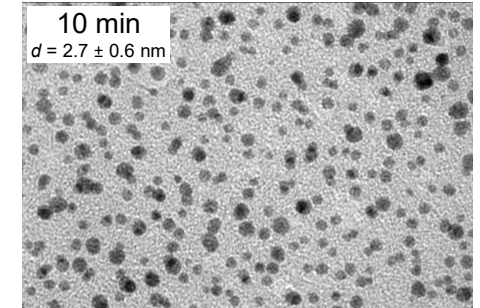
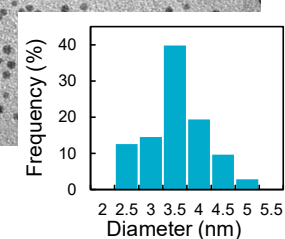
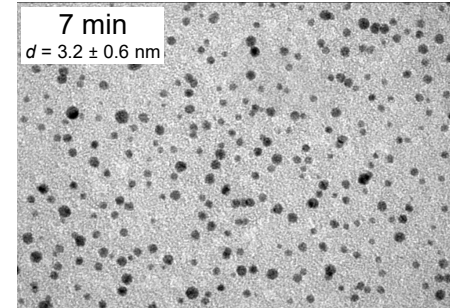
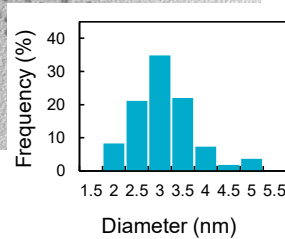
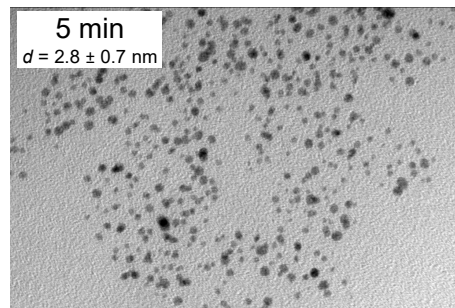
15 min after sputtering



4 weeks after sputtering

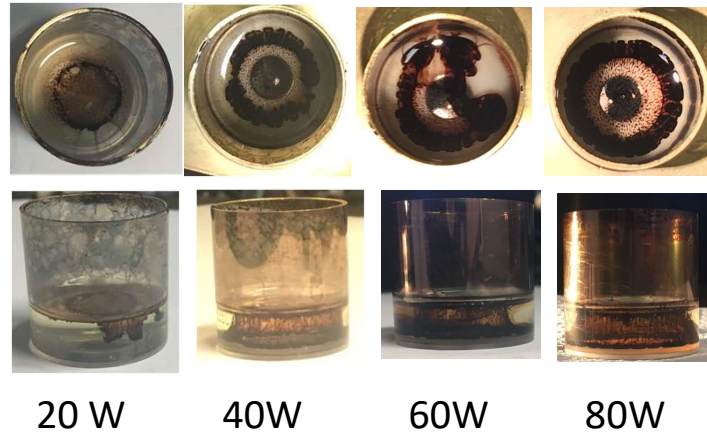


TEM analysis after 6 months



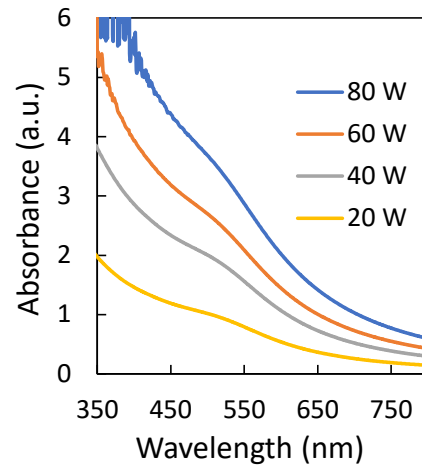
Effect of sputter power

Sputter time: 10 min

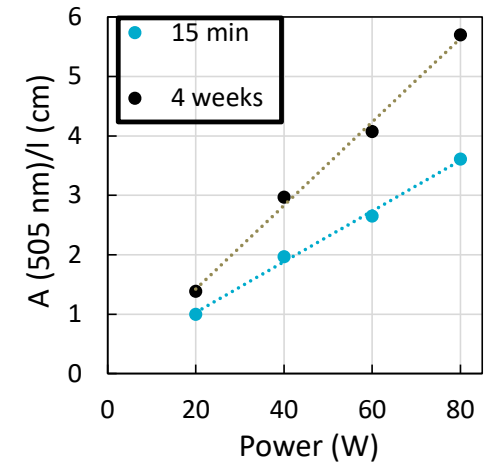
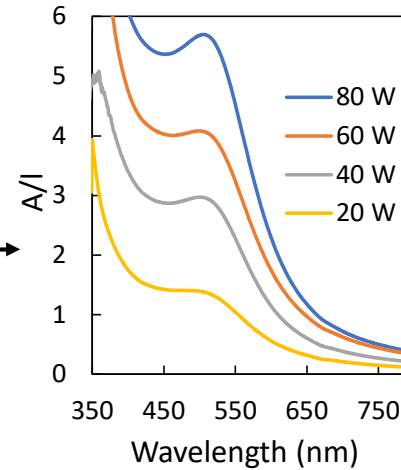


Ageing of the NP solutions

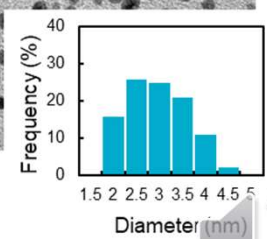
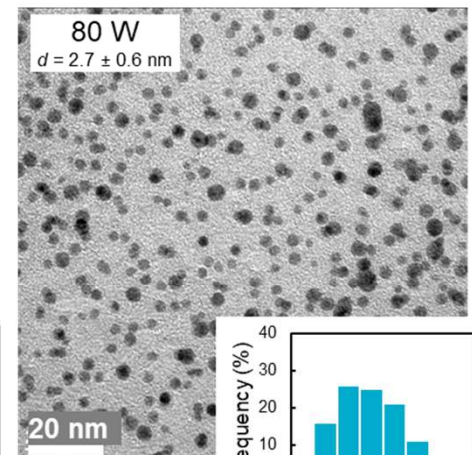
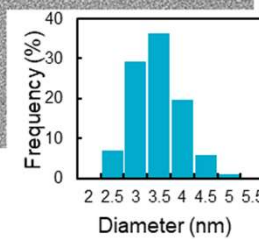
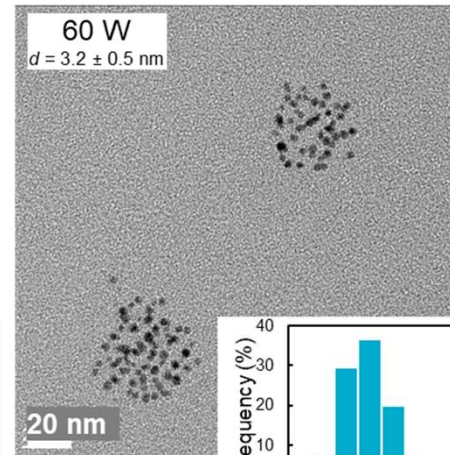
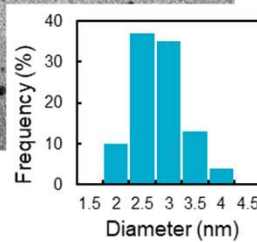
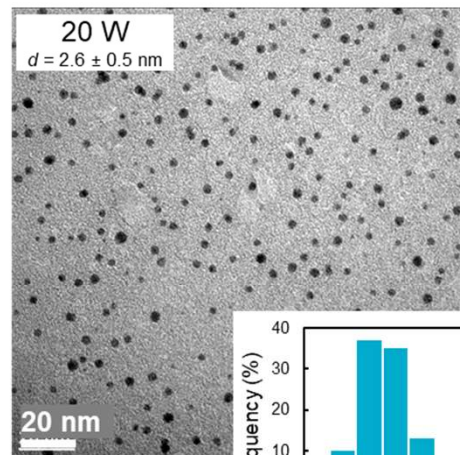
15 min after sputtering



4 weeks after sputtering



TEM analysis after 6 months



DC-MS vs. (unipolar) HiPIMS

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

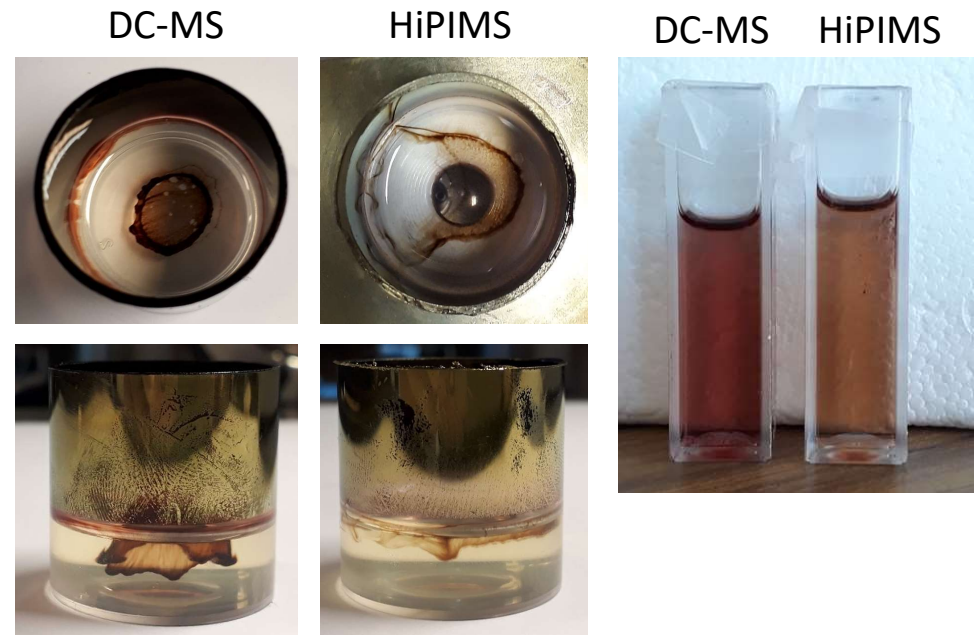
DC-MS:

$\Phi = (1.8 \pm 0.2) \cdot 10^{-7} \text{ moles/cm}^2 \cdot \text{minute}$

HiPIMS:

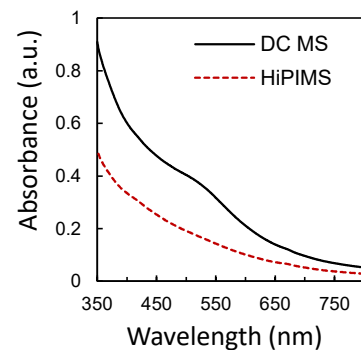
$T_{on} = 20 \mu\text{s}, I_{pk} = 0.3 \text{ A/cm}^2, f = 800 \text{ Hz},$

$\Phi = (0.9 \pm 0.1) \cdot 10^{-7} \text{ moles/cm}^2 \text{ min}$

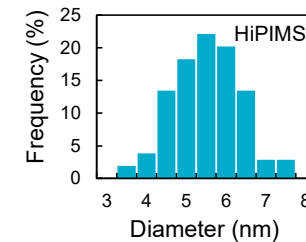
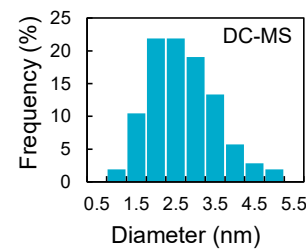
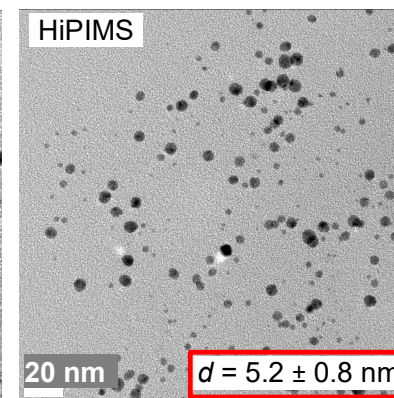
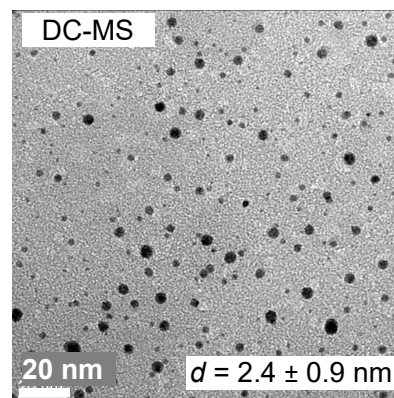
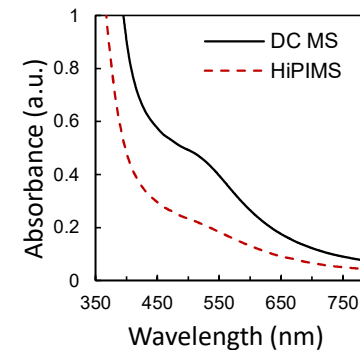


Ageing of the NP solutions

15 min after sputtering



6 weeks after sputtering



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

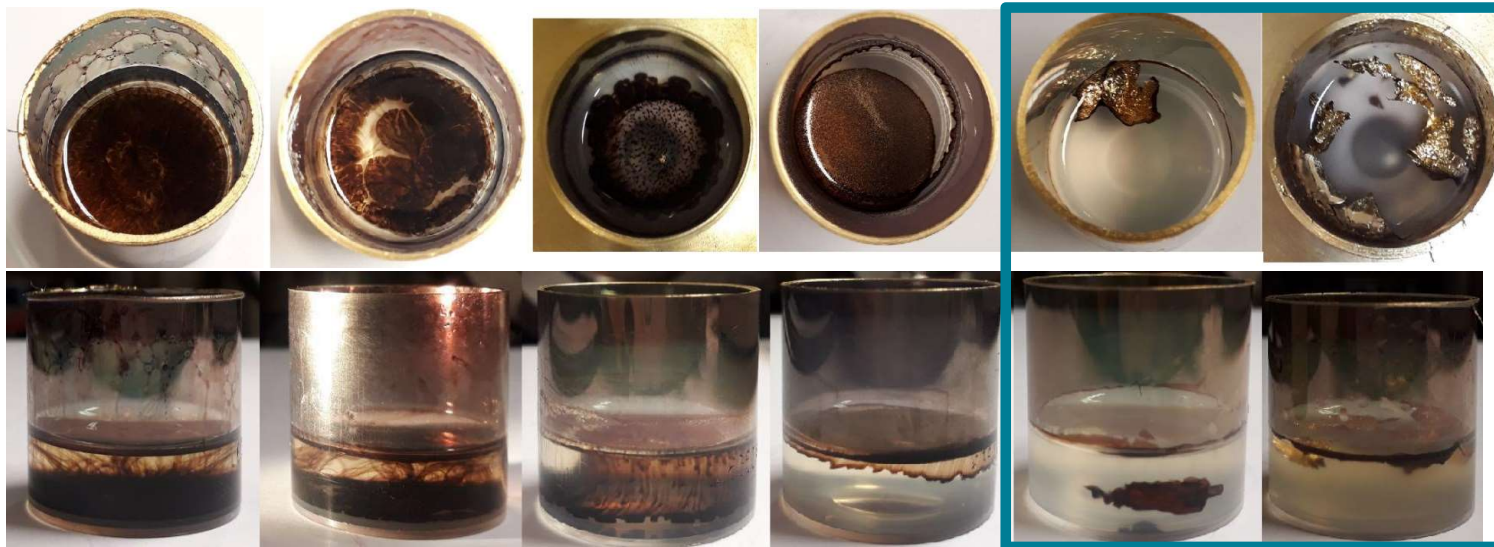
200

440

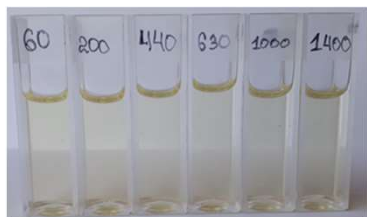
630

1000

1400



Surface tension
 $\sim 32.7 \text{ mJ} \cdot \text{m}^{-2}$



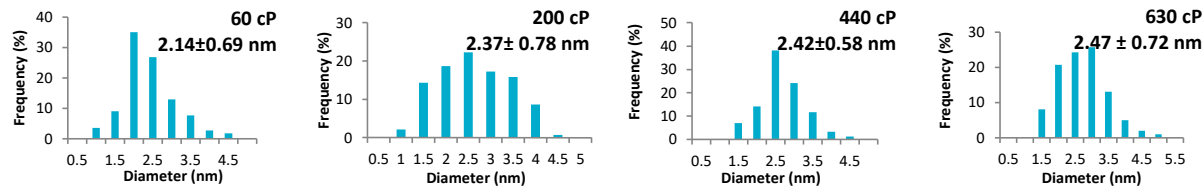
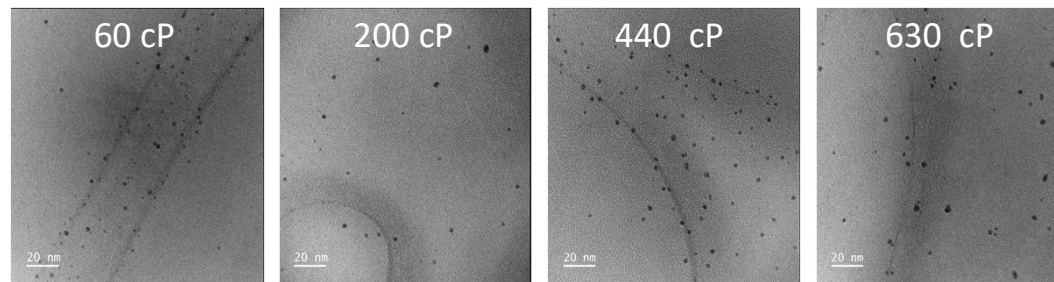
Viscosities (cP)

- Castor oil = 700 cP (35.1 mJ m^{-2})
- Water = 0.9 cP
- Honey $\sim 2000 - 10\,000$ 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

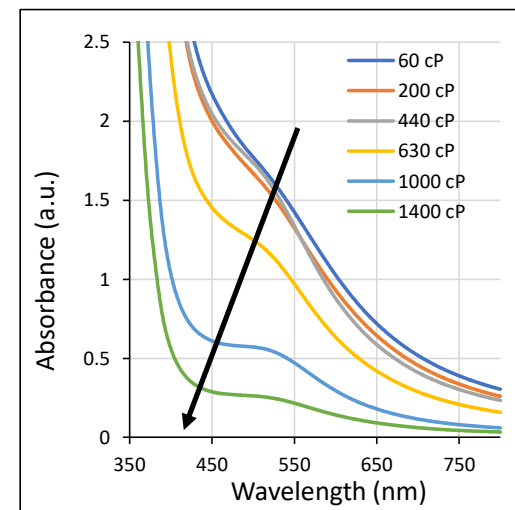
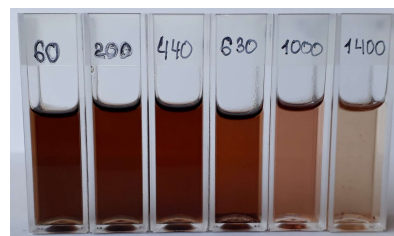
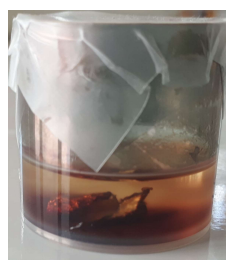
0.5 mTorr, 20 cm, 80 W, 10 min, substrate : polymerized rapeseed oil



5 months



Partial
dissolution



At higher viscosity

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



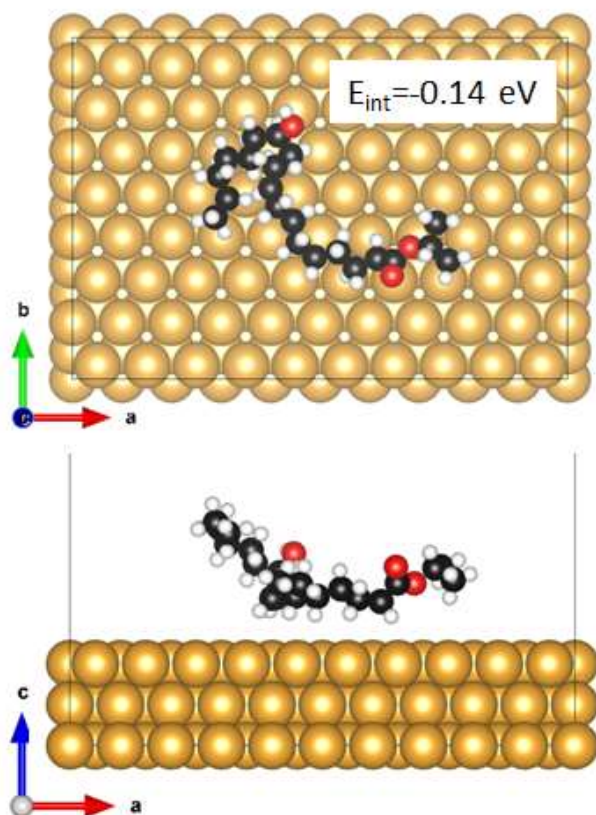
**What if we sputter silver
onto castor oil ?**



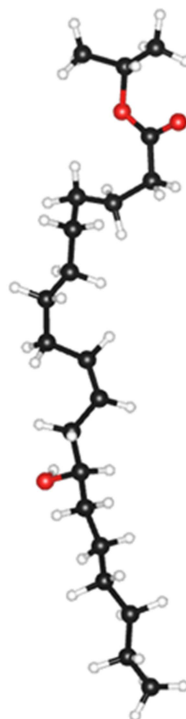
Metal surface – liquid interaction energy

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

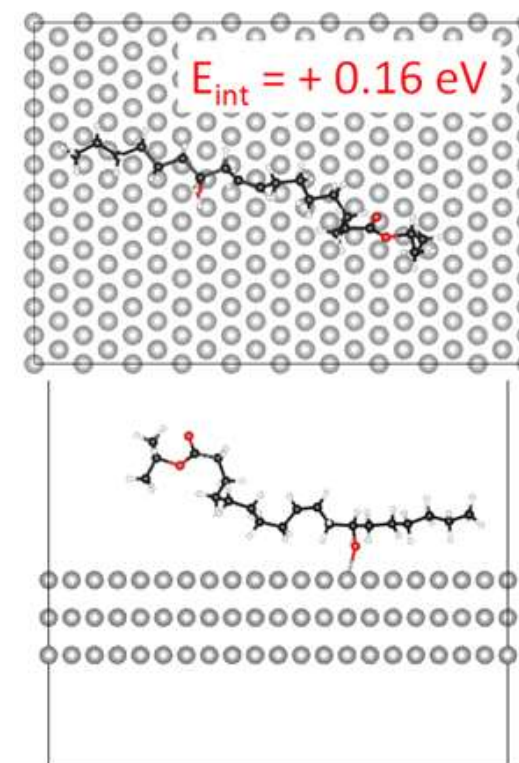
GOLD



1/3 of triglyceride
of ricinoleic acid



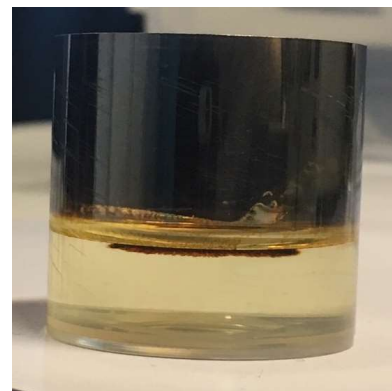
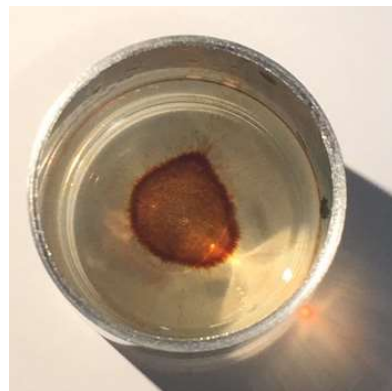
SILVER



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/cm²·min



Diapositive 19

SK9

size distribution, cristalinity ?

Stéphanos KONSTANTINIDIS; 03-05-21

Ui16

There is no size distributions for these particular 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.

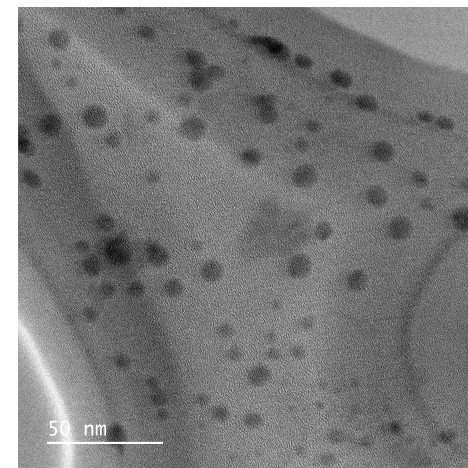
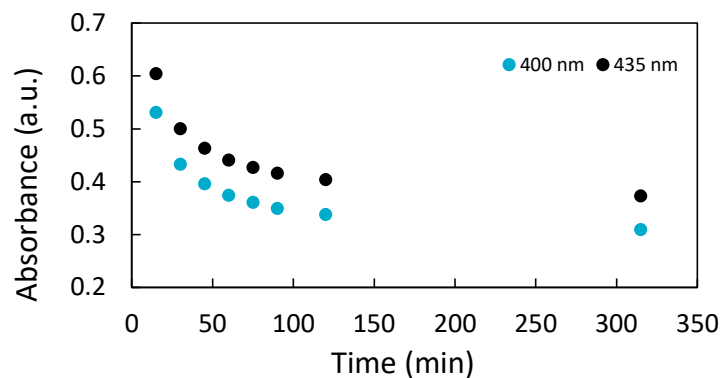
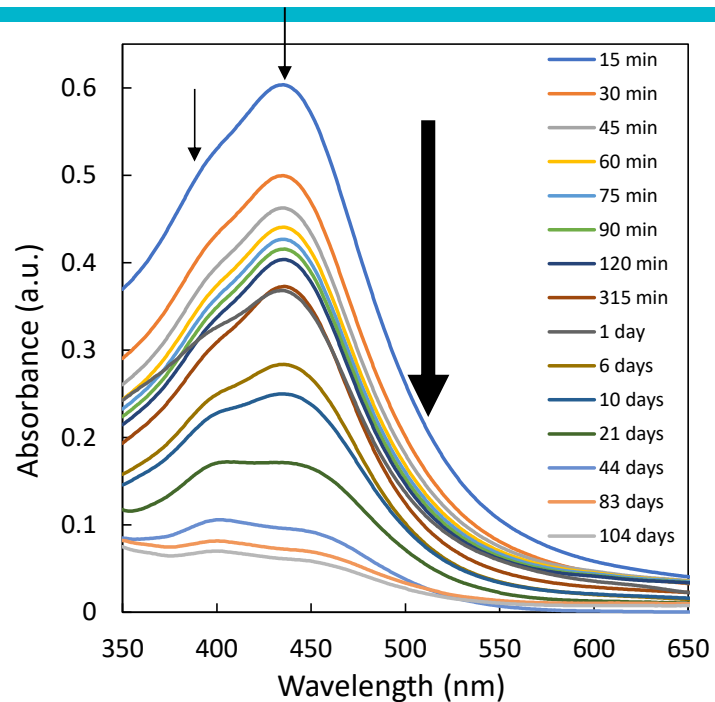
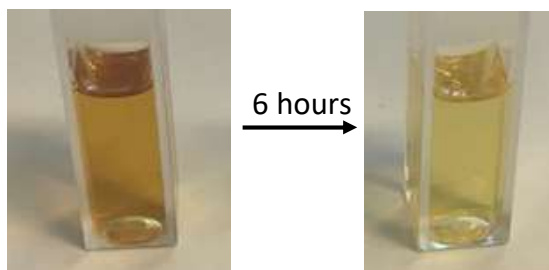
Utilisateur invité; 07-05-21

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 \pm 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: $(1.8 \pm 0.2) \cdot 10^{-7}$ moles/cm² min

Flux HiPIMS: $(0.9 \pm 0.1) \cdot 10^{-7}$ moles/cm² min

$f = 800$ Hz, $T_{ON,-} = 20$ μ s, $I_{pk} = 0.3$ A/cm²

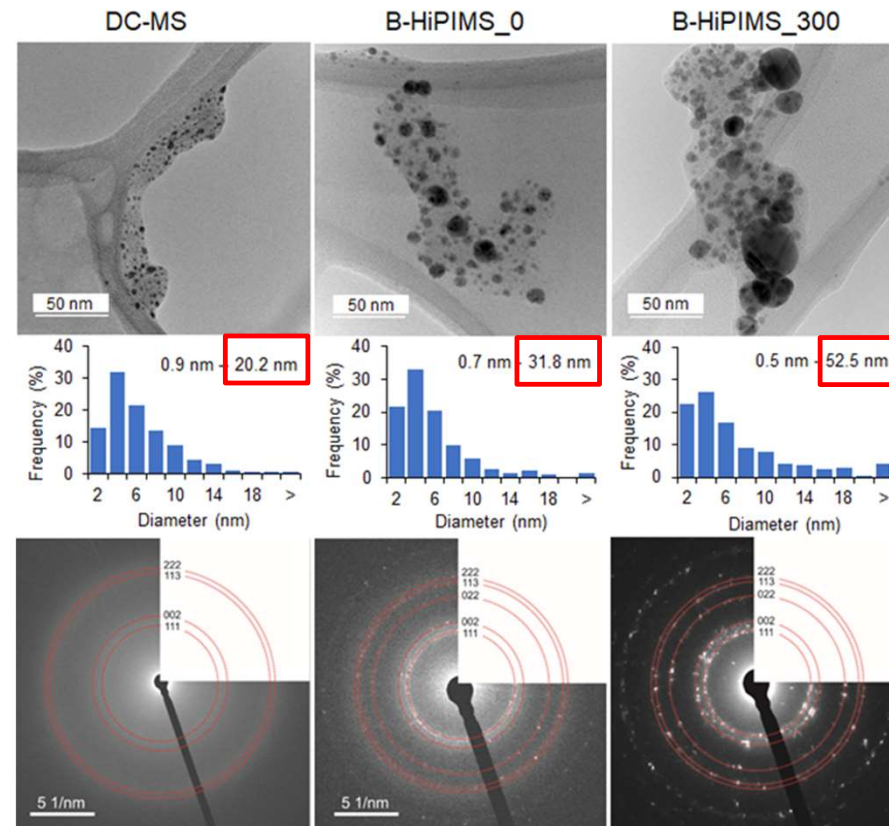
Flux B-HiPIMS: $(0.2 \pm 0.1) \cdot 10^{-7}$ moles/cm² min

$f = 800$ Hz, $T_{ON,-} = 20$ μ s, $I_{pk} = 0.3$ A/cm²

$V_+ = +300$ V, $T_{ON,+} = 250$ μ s, $T_{+/-} = 10$ μ s

Number of particles larger than 20 nm

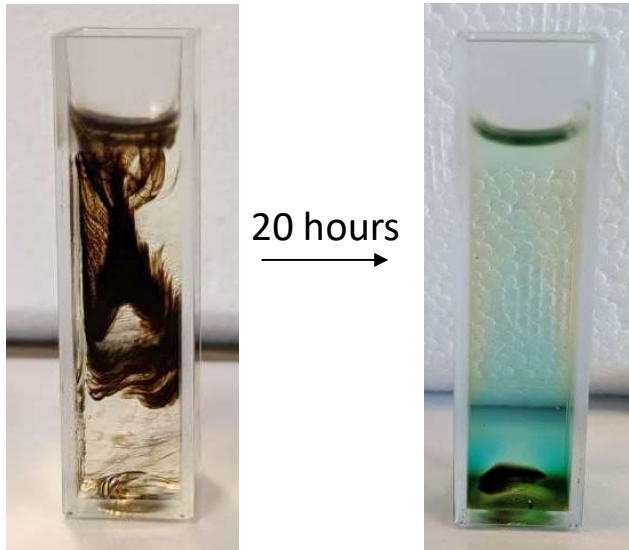
- 0.1% for DC-MS,
- 1.3 % for HiPIMS (B-HiPIMS_0)
- 4.2 % for bipolar HiPIMS (BHiPIMS_300)



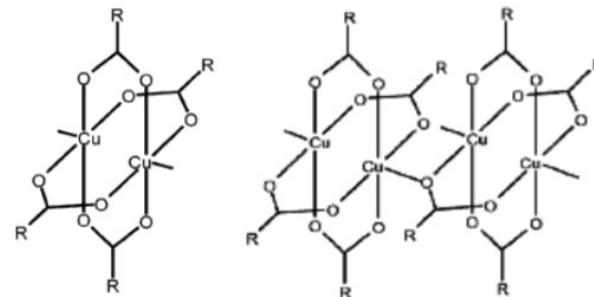
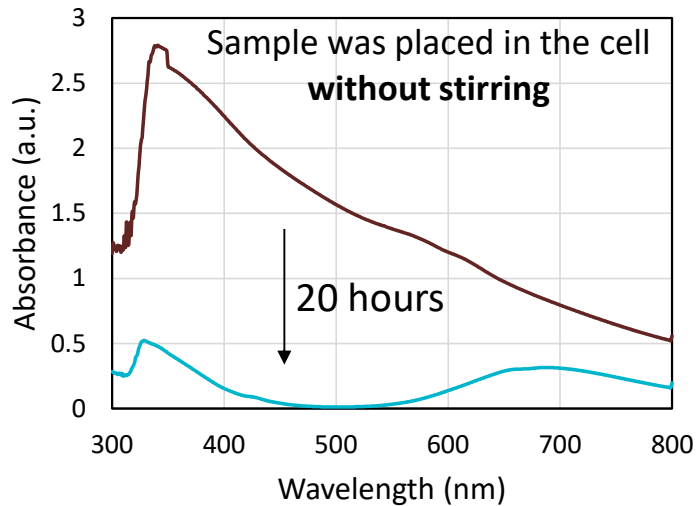
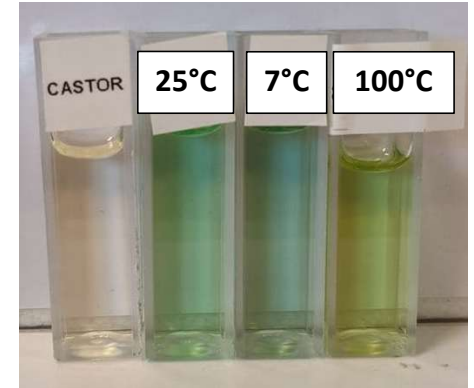
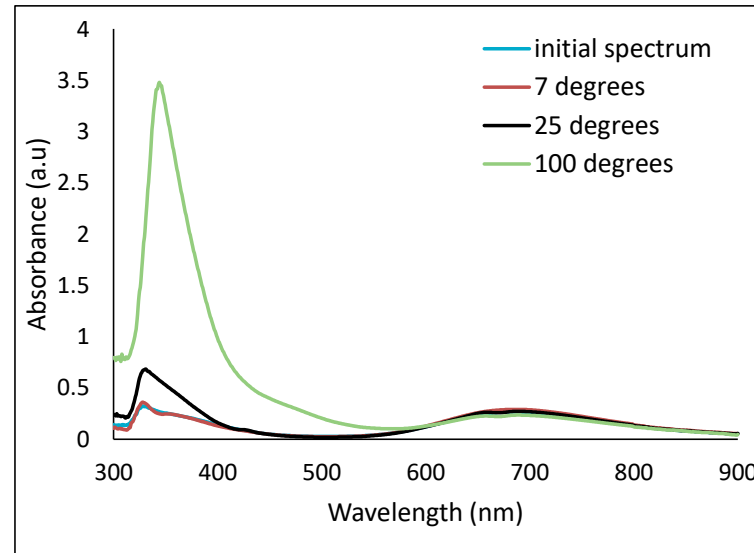
**What if we sputter Copper
onto castor oil ?**



Oxidation of Cu-NPs in castor oil

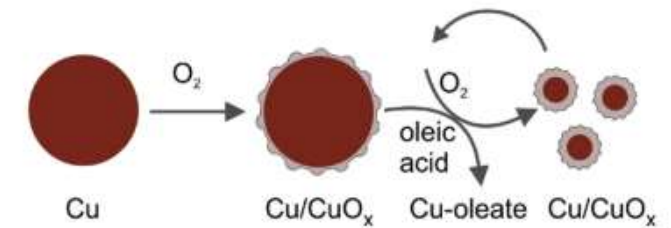


20 hours



Copper (II) oleate \longrightarrow 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).



- 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).

