

# 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

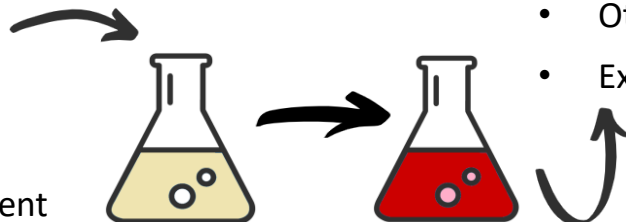
Periodic Table of the Elements

Atomic Number	Symbol	Name	Atomic Mass
1	H	Hydrogen	1.008
2	He	Helium	4.003
3	Li	Lithium	6.941
4	Be	Beryllium	9.012
5	B	Boron	10.811
6	C	Carbon	12.011
7	N	Nitrogen	14.007
8	O	Oxygen	15.999
9	F	Fluorine	18.998
10	Ne	Neon	20.180
11	Na	Sodium	22.990
12	Mg	Magnesium	24.305
13	Al	Aluminum	26.982
14	Si	Silicon	28.086
15	P	Phosphorus	30.974
16	S	Sulfur	32.065
17	Cl	Chlorine	35.453
18	Ar	Argon	39.948
19	K	Potassium	39.098
20	Ca	Calcium	40.078
21	Sc	Scandium	44.956
22	Ti	Titanium	47.88
23	V	Vanadium	50.942
24	Cr	Chromium	51.996
25	Mn	Manganese	54.938
26	Fe	Iron	55.845
27	Co	Cobalt	58.933
28	Ni	Nickel	58.693
29	Cu	Copper	63.546
30	Zn	Zinc	65.38
31	Ga	Gallium	69.723
32	Ge	Germanium	72.63
33	As	Arsenic	74.922
34	Se	Selenium	78.972
35	Br	Bromine	79.904
36	Kr	Krypton	83.80
37	Rb	Rubidium	85.468
38	Sr	Strontium	87.62
39	Y	Yttrium	88.906
40	Zr	Zirconium	91.224
41	Nb	Niobium	92.906
42	Mo	Molybdenum	95.94
43	Tc	Technetium	98.907
44	Ru	Ruthenium	101.07
45	Rh	Rhodium	101.06
46	Pd	Palladium	106.36
47	Ag	Silver	107.868
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	132.905
56	Ba	Barium	137.327
57	La	Lanthanum	138.905
58	Ce	Cerium	140.12
59	Pr	Praseodymium	140.908
60	Nd	Neodymium	144.24
61	Pm	Promethium	144.913
62	Sm	Samarium	150.36
63	Eu	Europium	151.964
64	Gd	Gadolinium	157.25
65	Tb	Terbium	158.925
66	Dy	Dysprosium	162.50
67	Ho	Holmium	164.930
68	Er	Erbium	167.26
69	Tm	Thulium	168.934
70	Yb	Ytterbium	173.054
71	Lu	Lutetium	174.967
72	Hf	Hafnium	178.49
73	Ta	Tantalum	180.948
74	W	Tungsten	183.85
75	Re	Rhenium	186.207
76	Os	Osmium	190.23
77	Ir	Iridium	192.22
78	Pt	Platinum	195.08
79	Au	Gold	196.967
80	Hg	Mercury	200.59
81	Tl	Thallium	204.38
82	Pb	Lead	207.2
83	Bi	Bismuth	208.98
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	289
111	Rg	Roentgenium	290
112	Cn	Copernicium	285
113	Uut	Ununtrium	288
114	Fl	Flerovium	289
115	Uup	Ununpentium	288
116	Lv	Livermorium	293
117	Uus	Ununseptium	289
118	Uu	Ununoctium	289

+ O<sub>2</sub> / N<sub>2</sub> / ...

### Classic colloidal synthesis

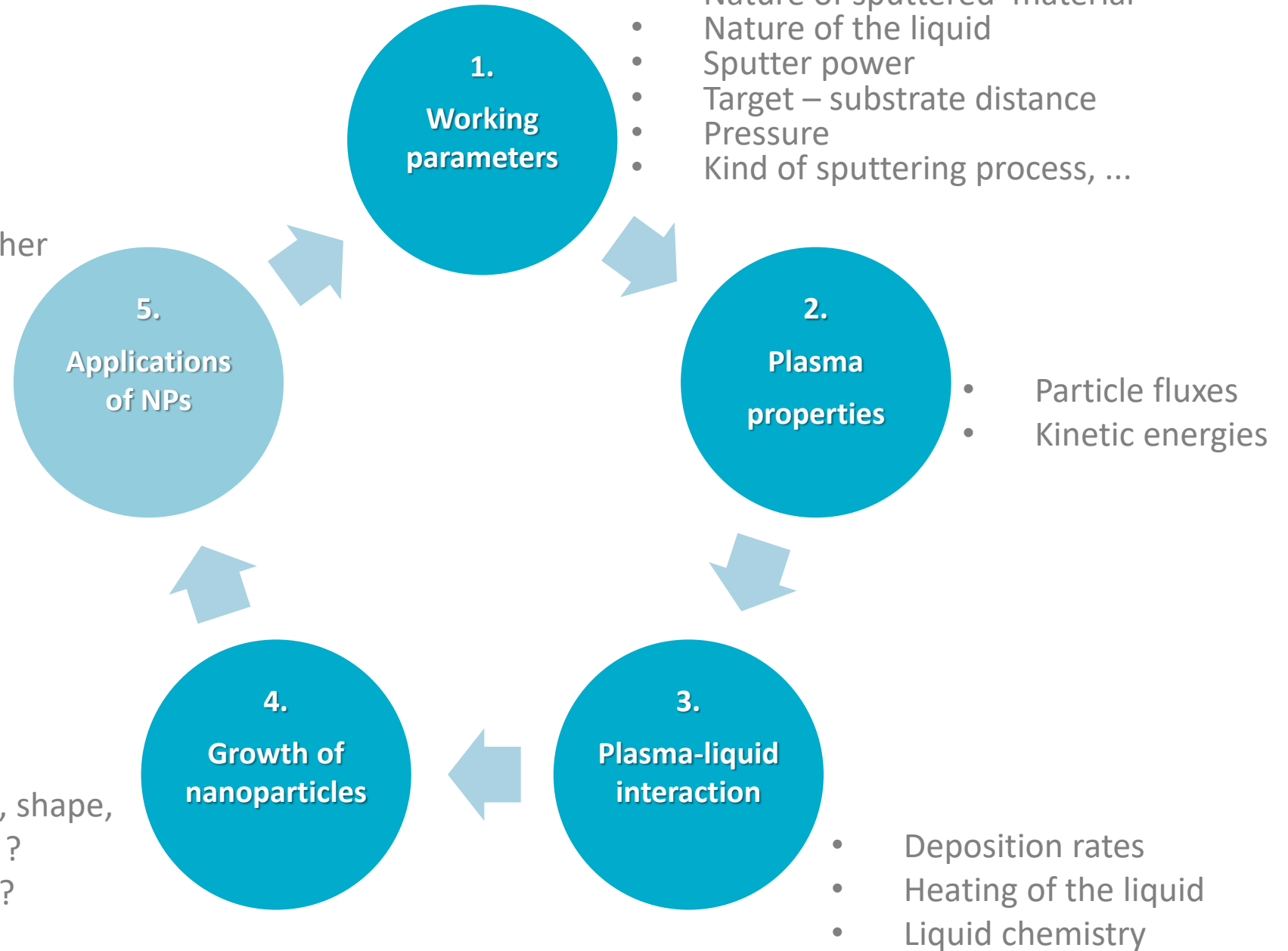
- Solvent
- Metal salt
- Reducer
- Capping agent



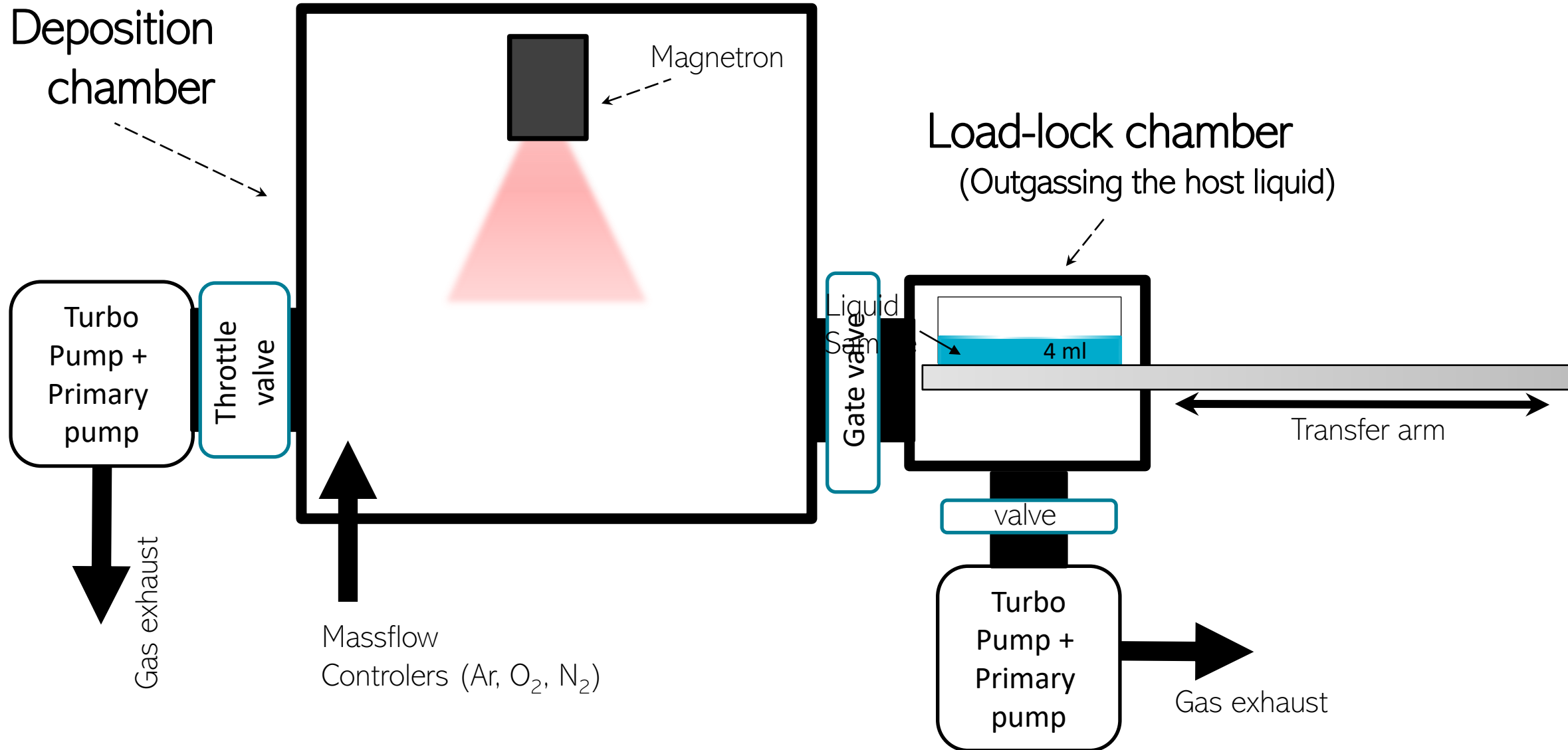
- Nanoparticles
- Other reaction products
- Excess of reagents

# Our goal

- Collaborations with other research groups



# Experimental set-up



# Castor oil as a host liquid



Ricinus communis

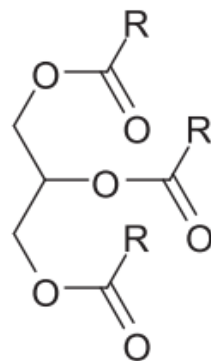
Castor beans



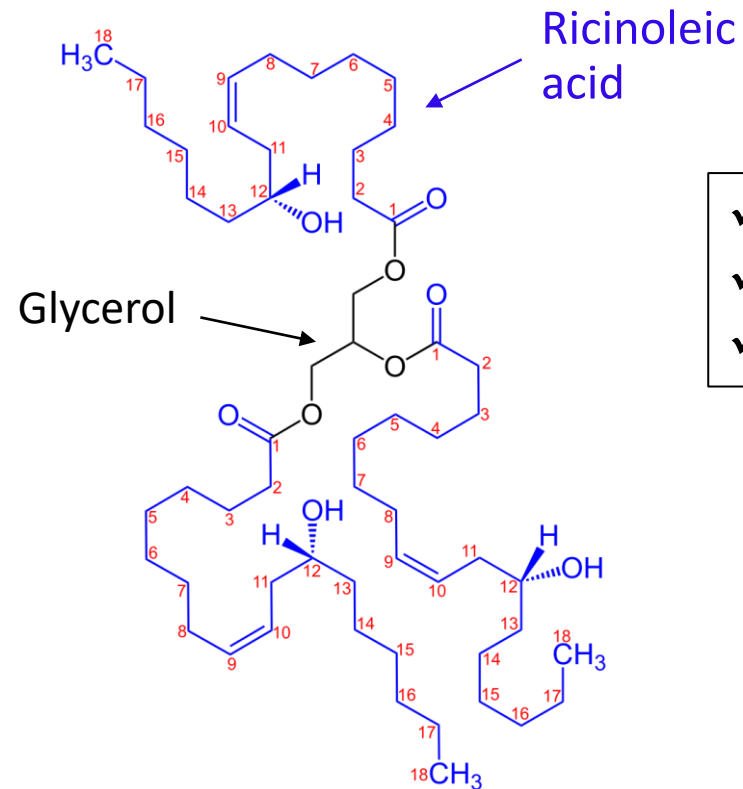
Castor oil = mixture of triglycerides

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

Generic Triglyceride



Ricinoleate



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

# 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)

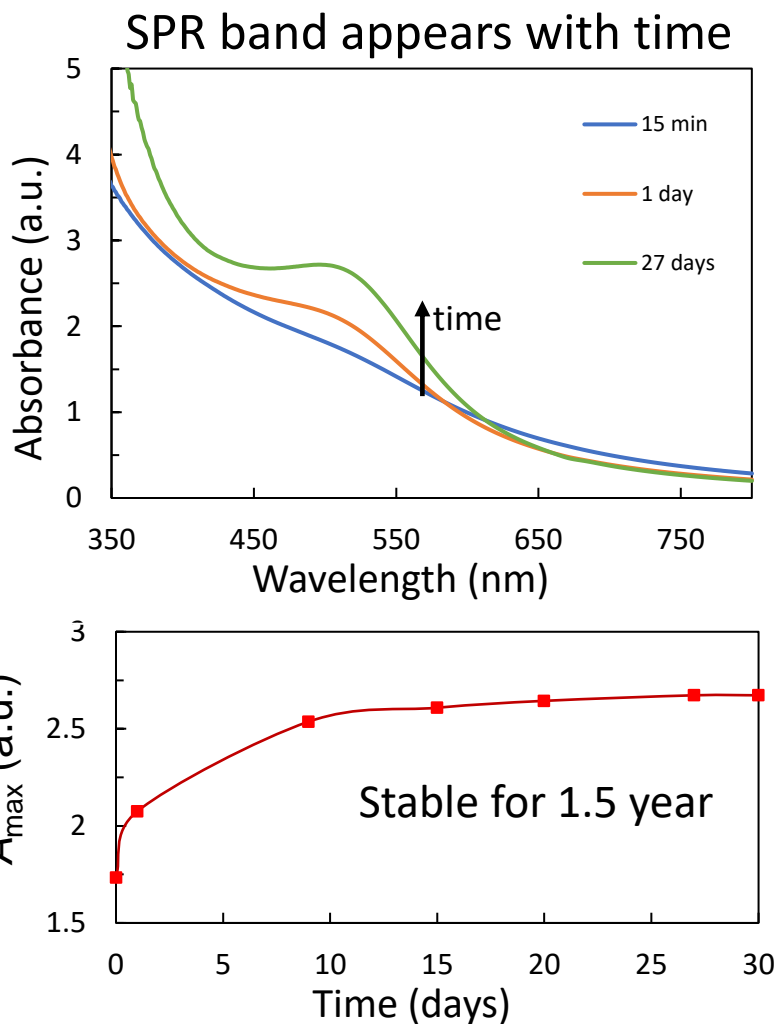
Methods of NP characterization:

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

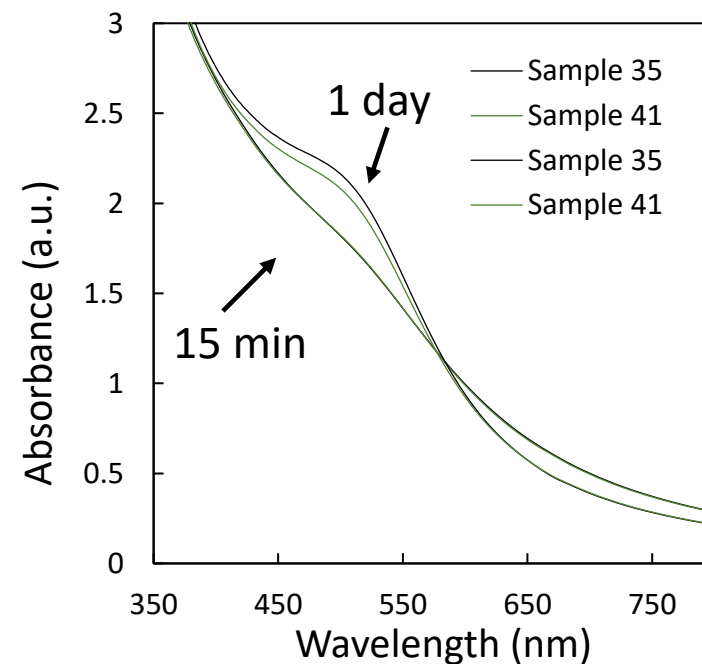
# 1. Sputtering Gold on Castor oil

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

$p_{\text{Ar}} = 0.5 \text{ mTorr}$ ,  $\text{WD} = 20 \text{ cm}$ ,  $t_s = 5 \text{ min}$ ,  $P = 80 \text{ W} \rightarrow \text{Flux of metal atoms} : \Phi = (2.5 \pm 0.5) \cdot 10^{-7} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$

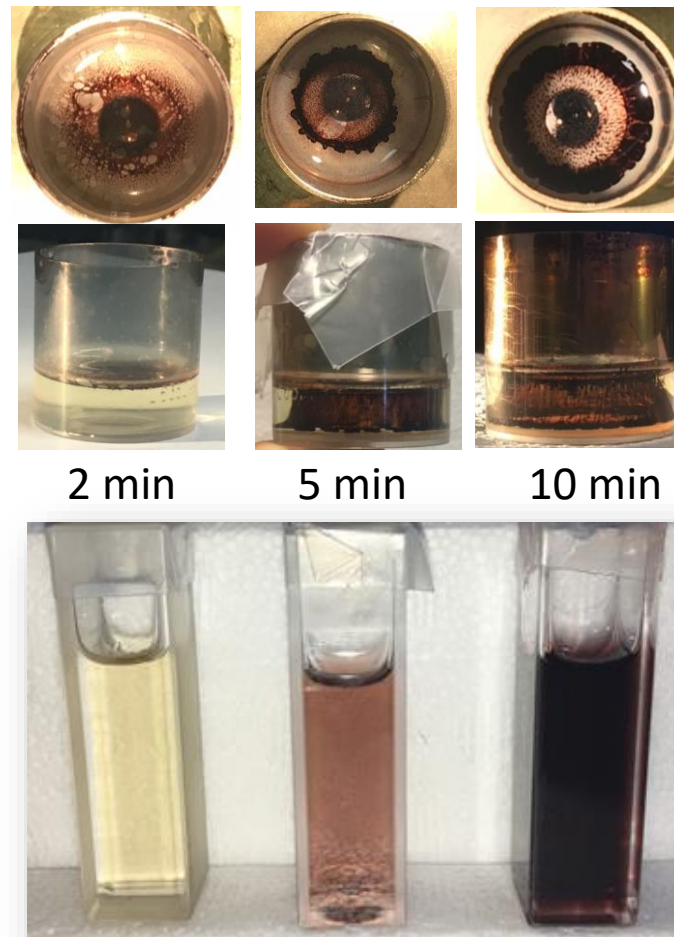


- NP continue to grow for a few days after sputtering
- NP solutions are stable for a very long time
- Good reproducibility





# Effect of sputter time



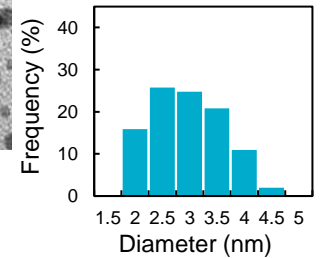
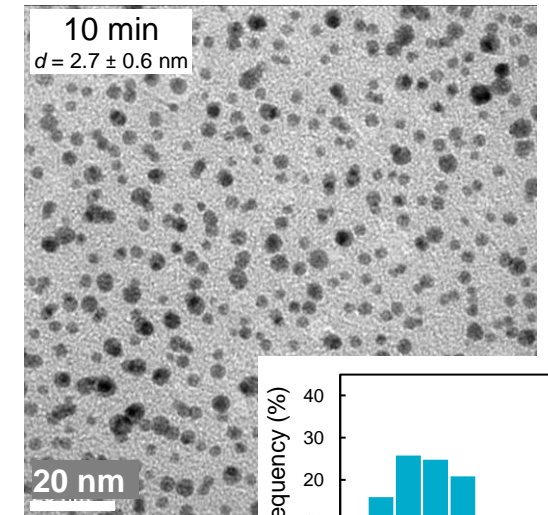
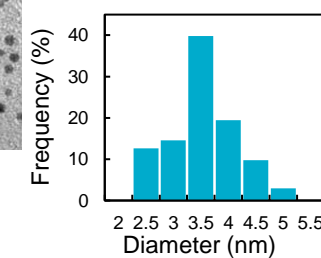
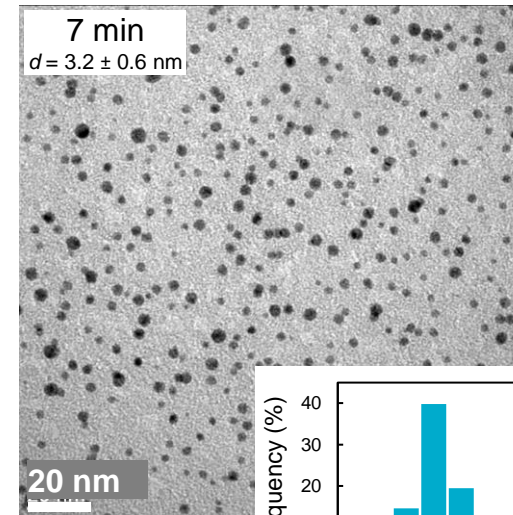
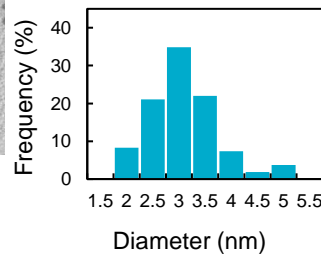
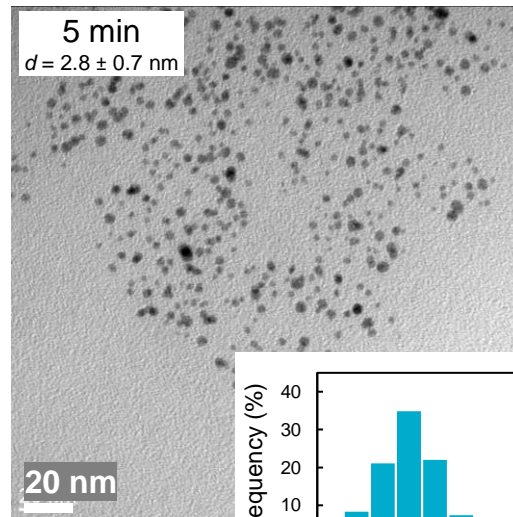
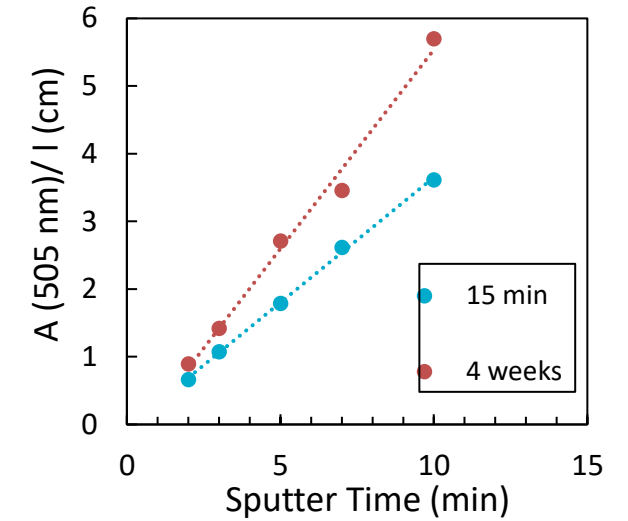
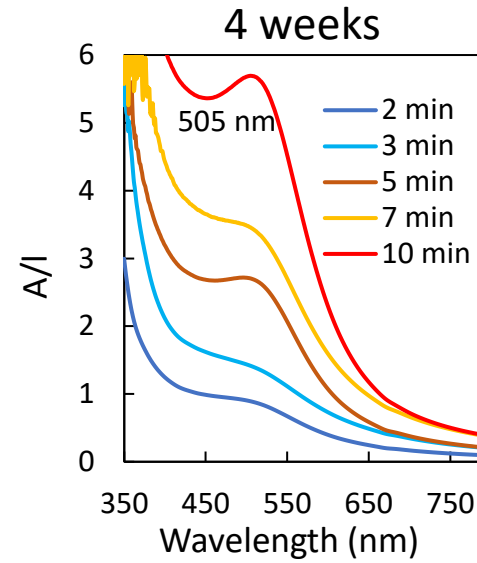
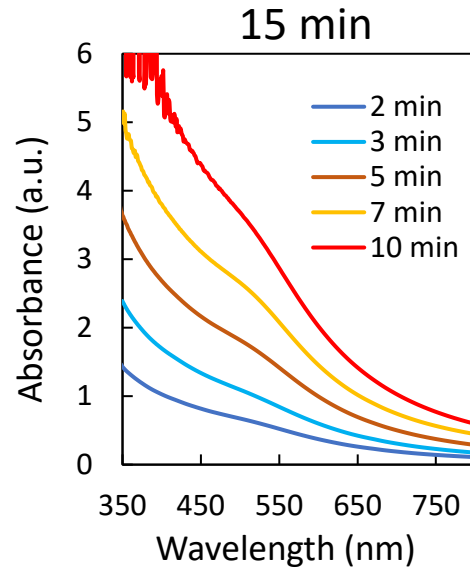
2 min

5 min

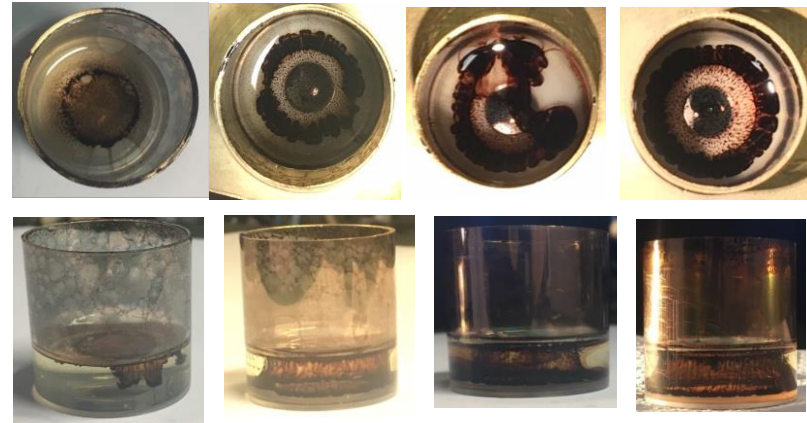
10 min

$p_{\text{Ar}} = 0.5 \text{ mTorr}$ ,  $\text{WD} = 20 \text{ cm}$ ,  $P = 80 \text{ W}$ ,  $\rightarrow$  Flux of metal atoms :  $\Phi = (2.5 \pm 0.5) \cdot 10^{-7} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$

# Different deposition times: ageing of the NP solutions



# Effect of sputter power

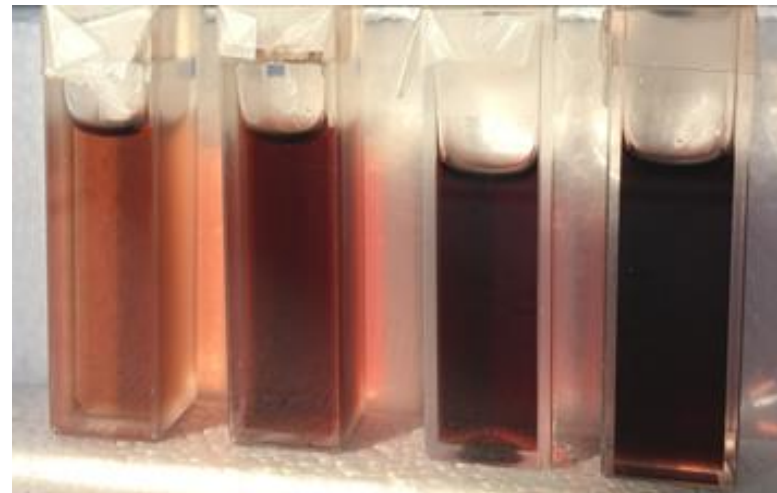


20 W

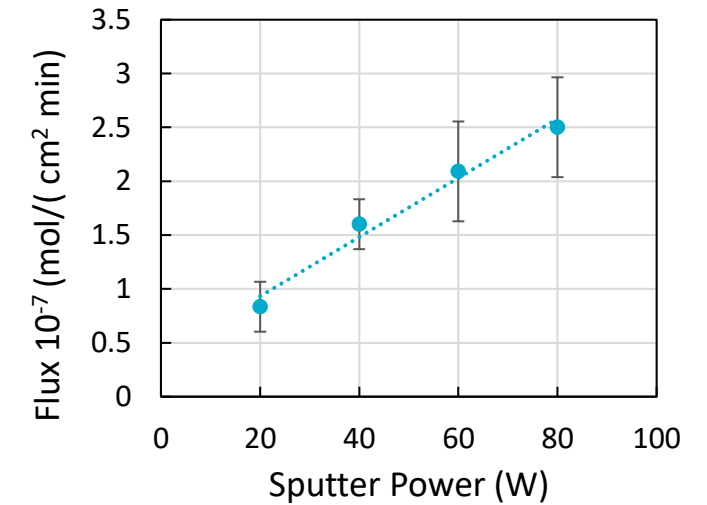
40W

60W

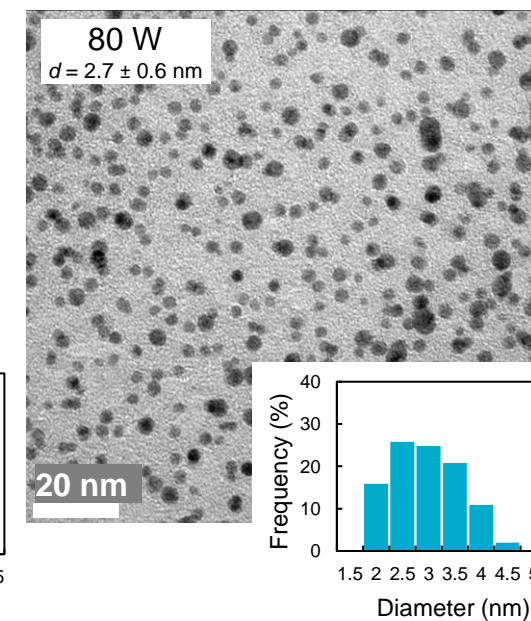
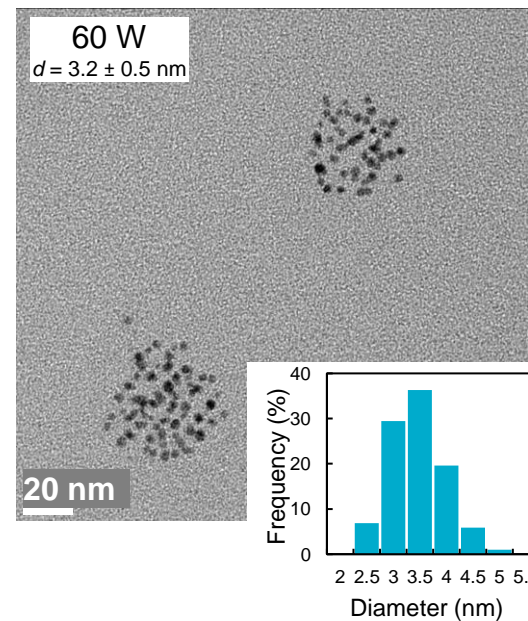
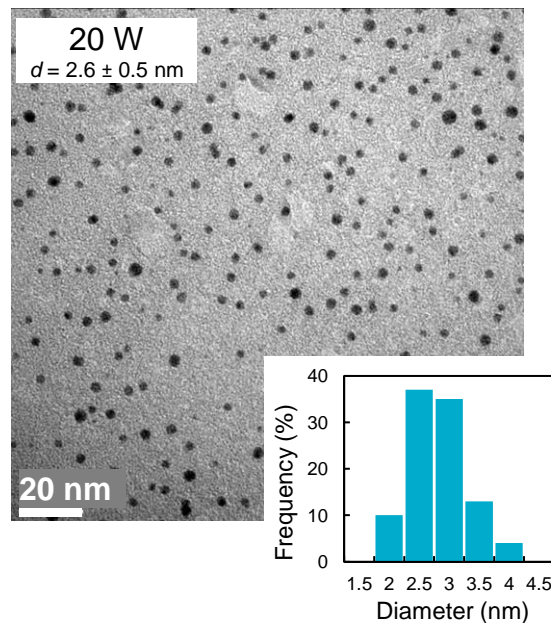
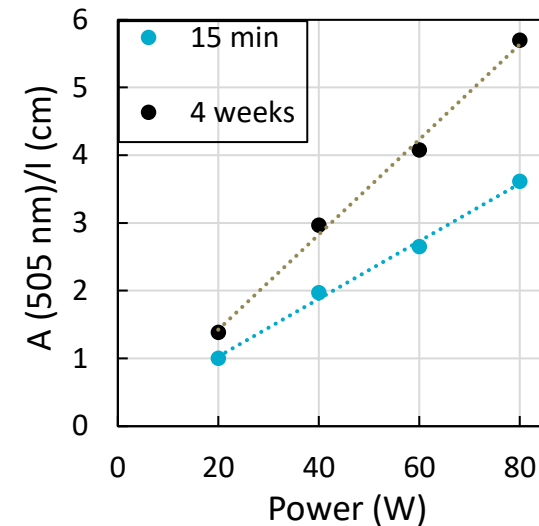
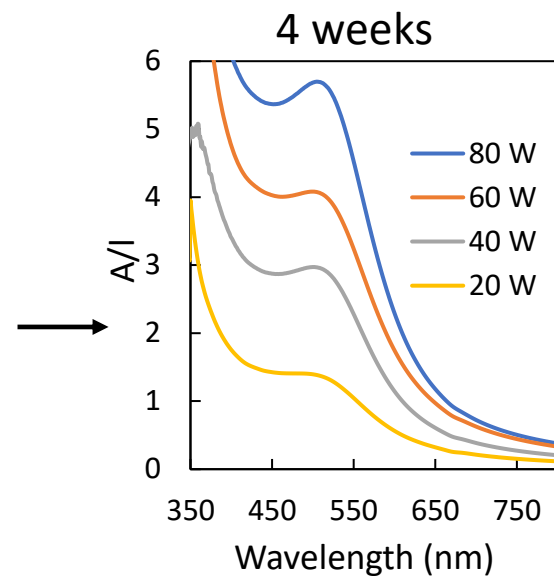
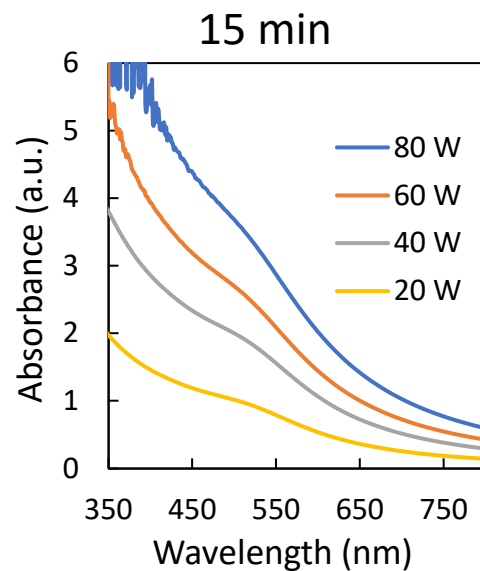
80W



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



# Different sputter powers : ageing of the NP solutions



# DC-MS vs. (unipolar) HiPIMS

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

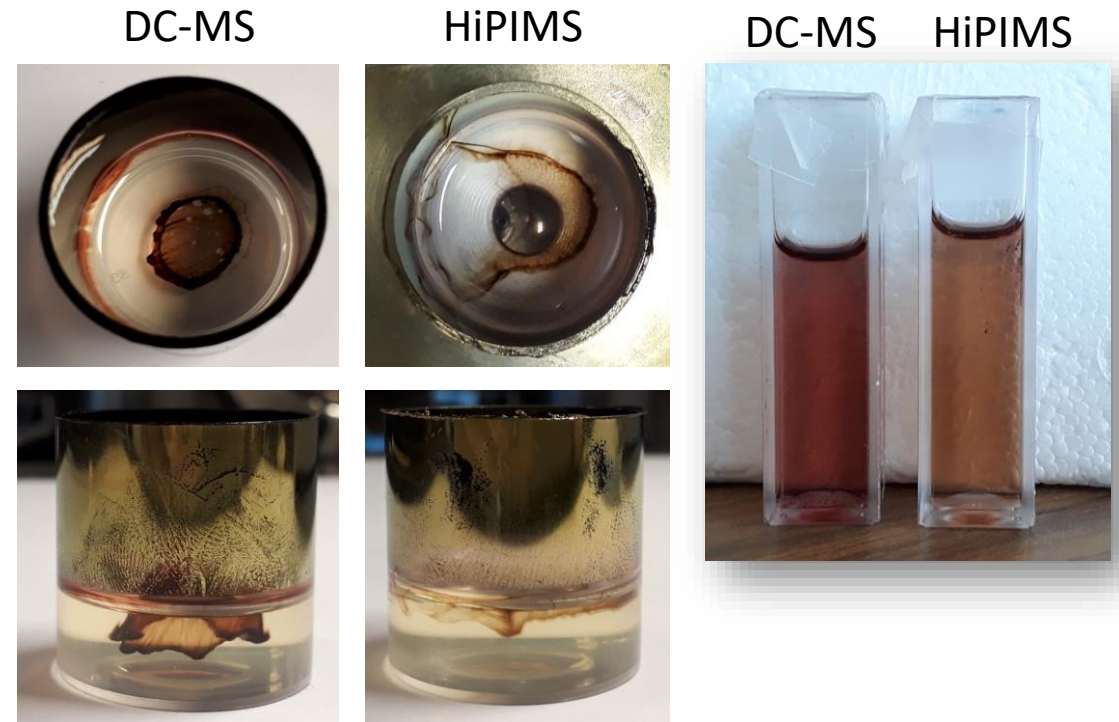
DC-MS:

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

HiPIMS:

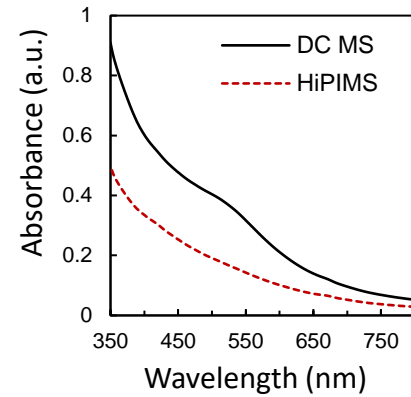
$T_{\text{on}} = 20 \mu\text{s}, I_{\text{pk}} = 0.3 \text{ A/cm}^2, f = 800 \text{ Hz},$

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

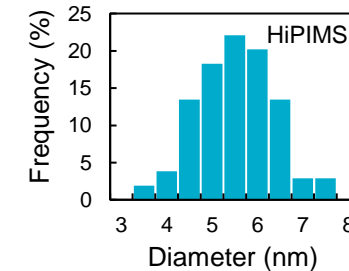
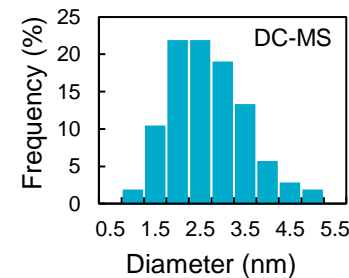
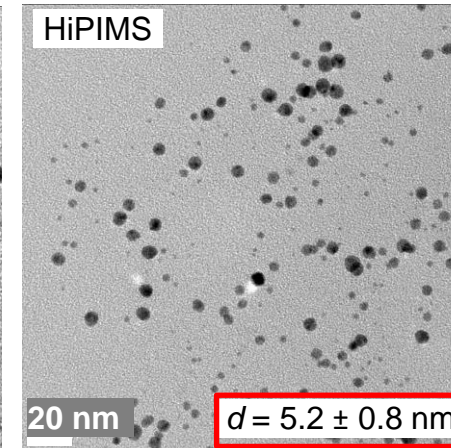
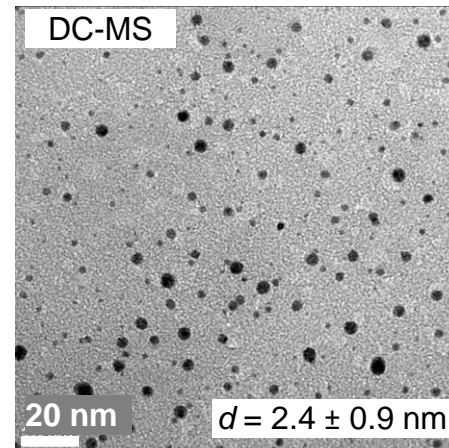
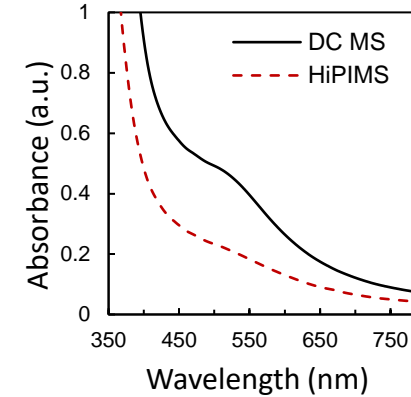


# Ageing of the NP solutions

15 min after sputtering

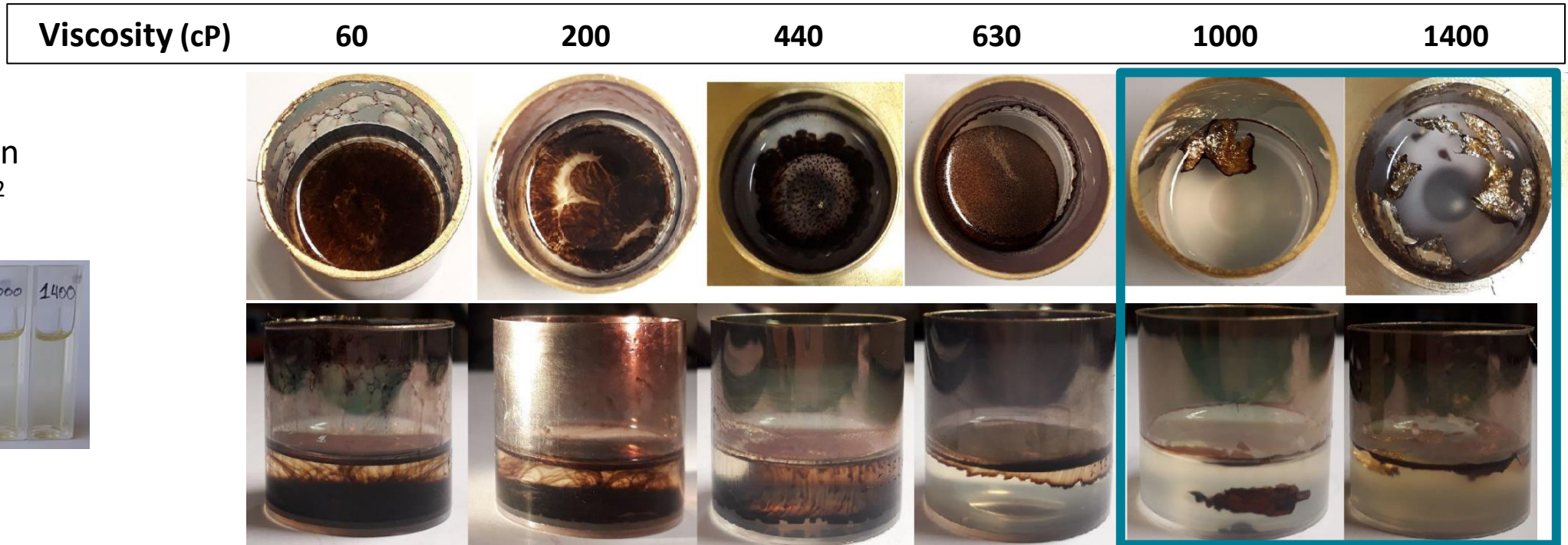


6 weeks after sputtering

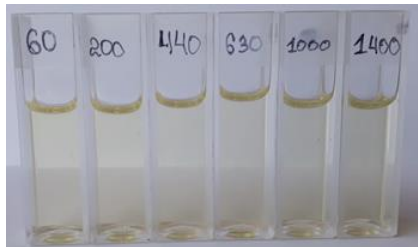


# Effect of the liquid viscosity

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



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

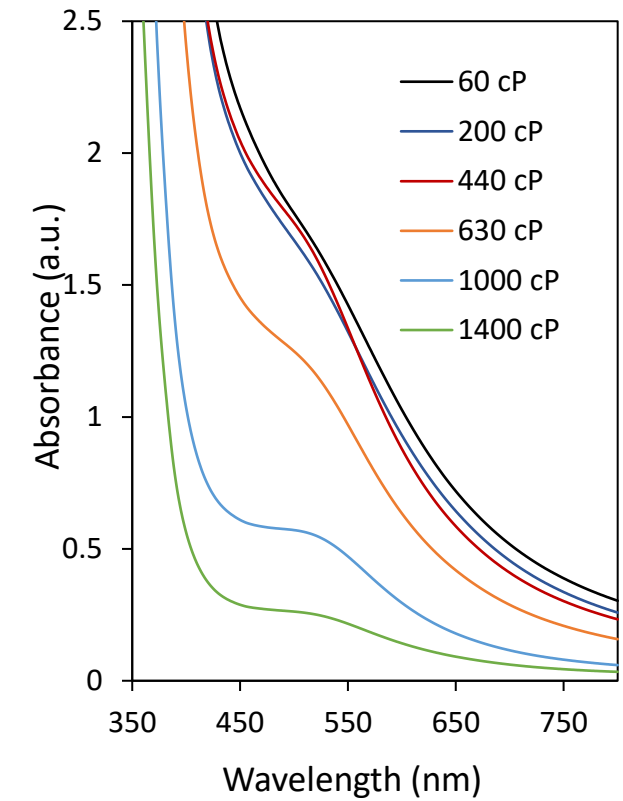
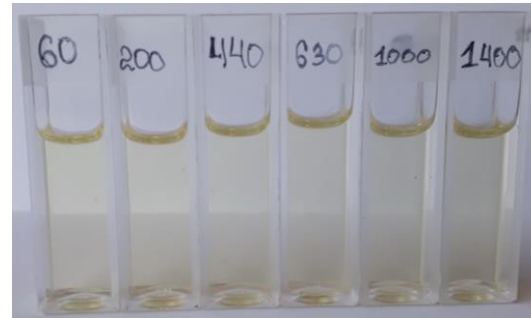
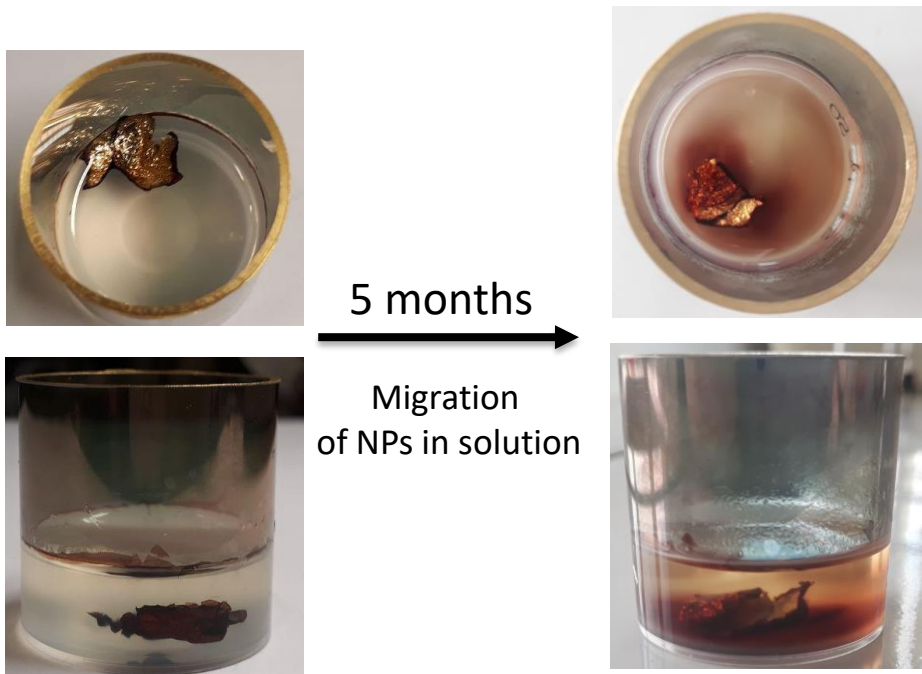


Viscosities (cP)

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

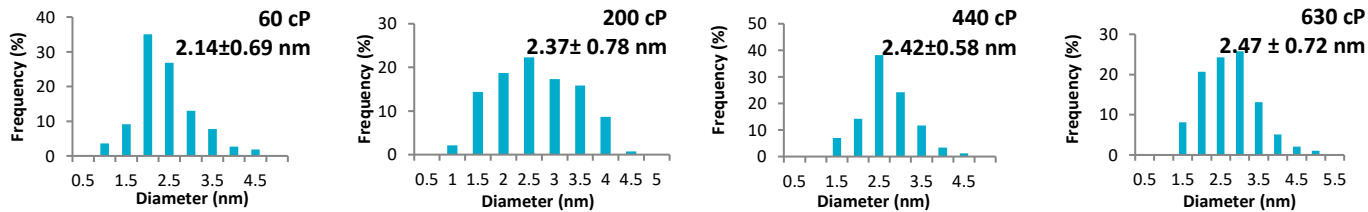
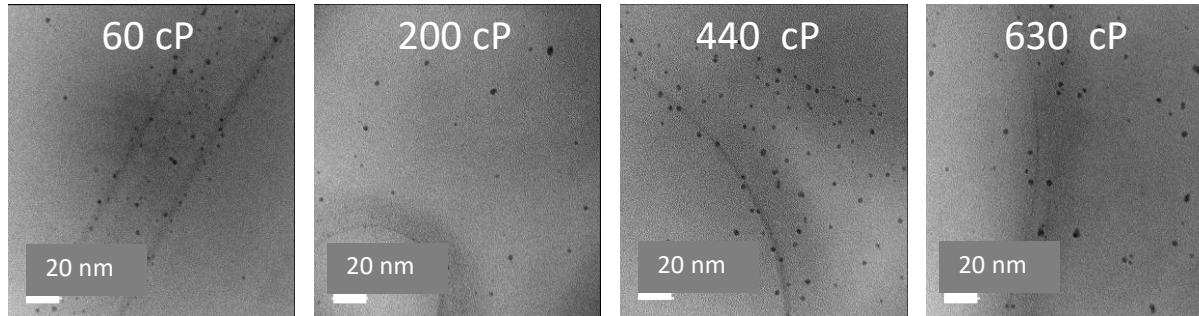
Film is obtained  
like on a solid surface

# Effect of the liquid viscosity

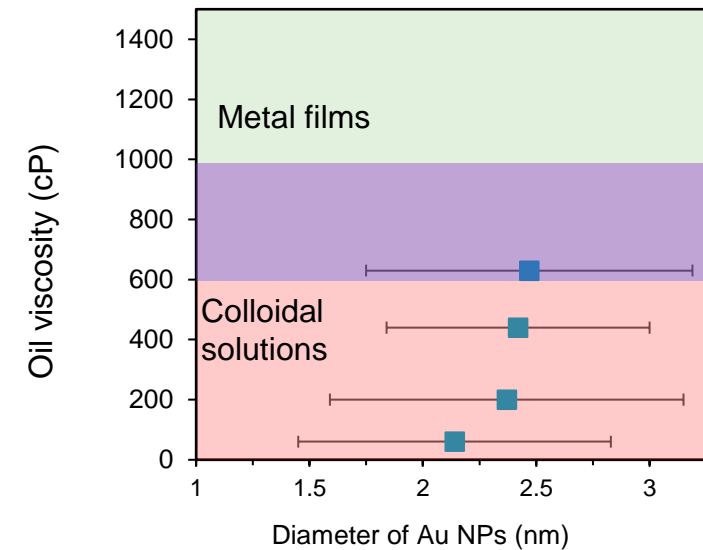




# Effect of the host liquid viscosity



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) =  $(10 \pm 1)$  nm  
 $d_{Au}$  (1400 cP) =  $(13 \pm 2)$  nm

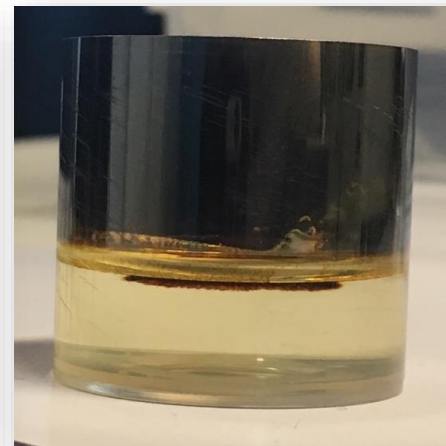
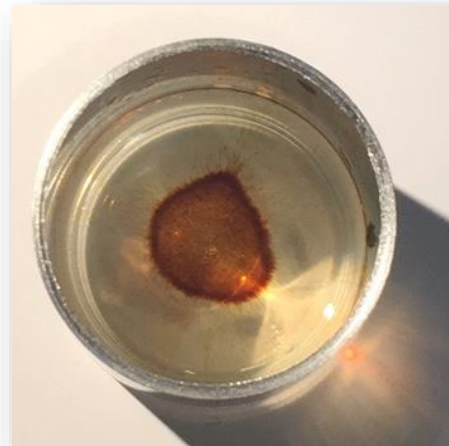


## **2. What if we sputter silver onto castor oil ?**

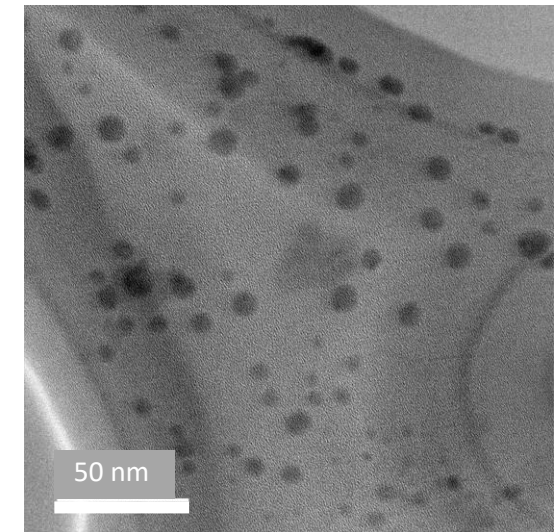
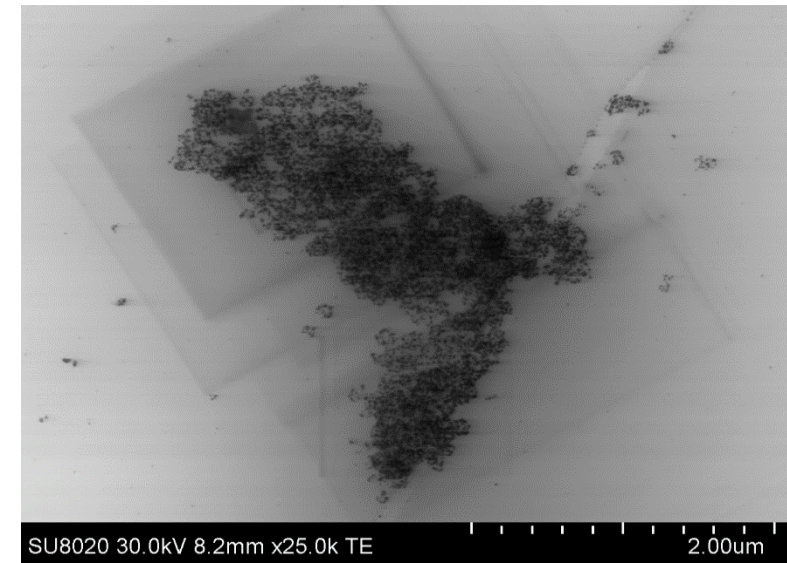
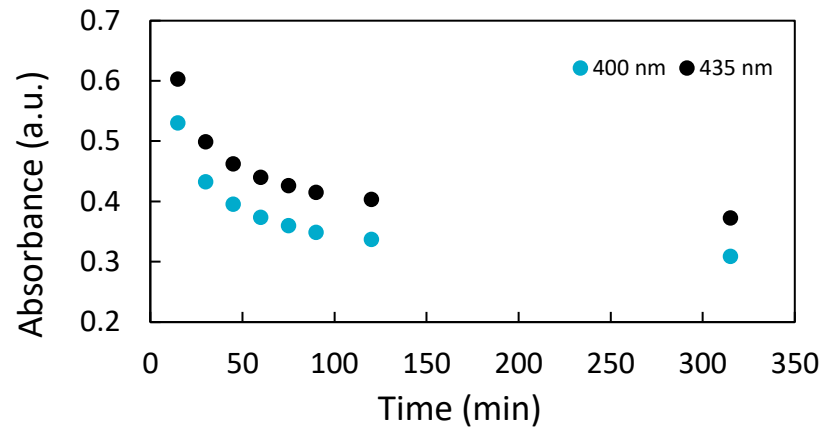
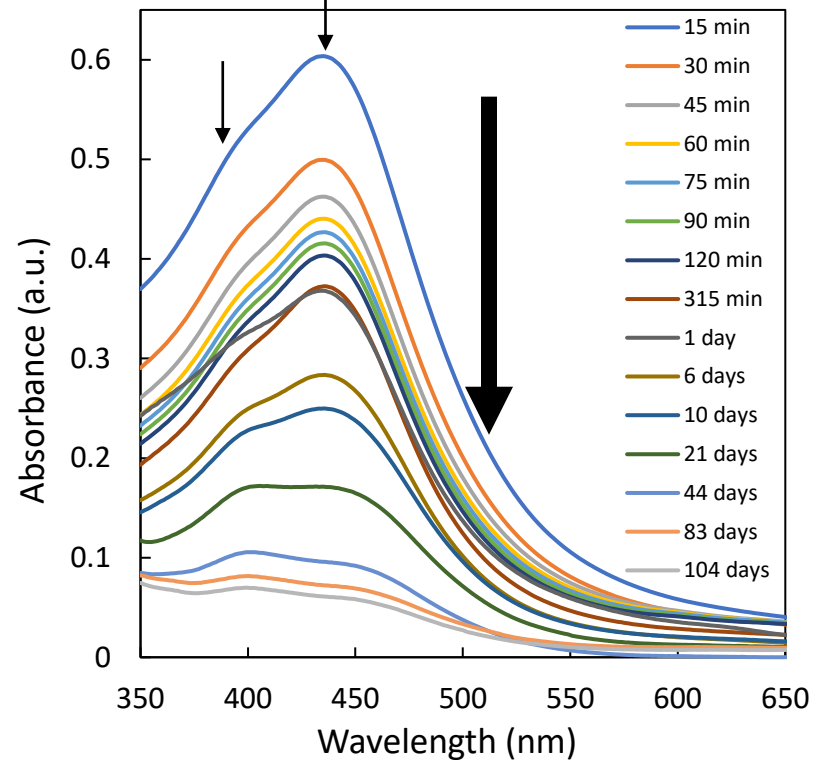
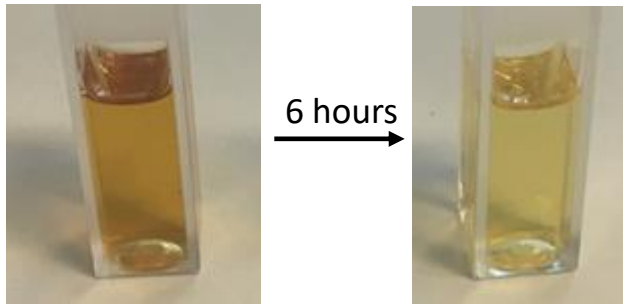
# DC-MS of silver target onto castor oil

0.5 mTorr, 20 cm, 80 W, 3 min

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



# Ageing of the Ag-NP solutions

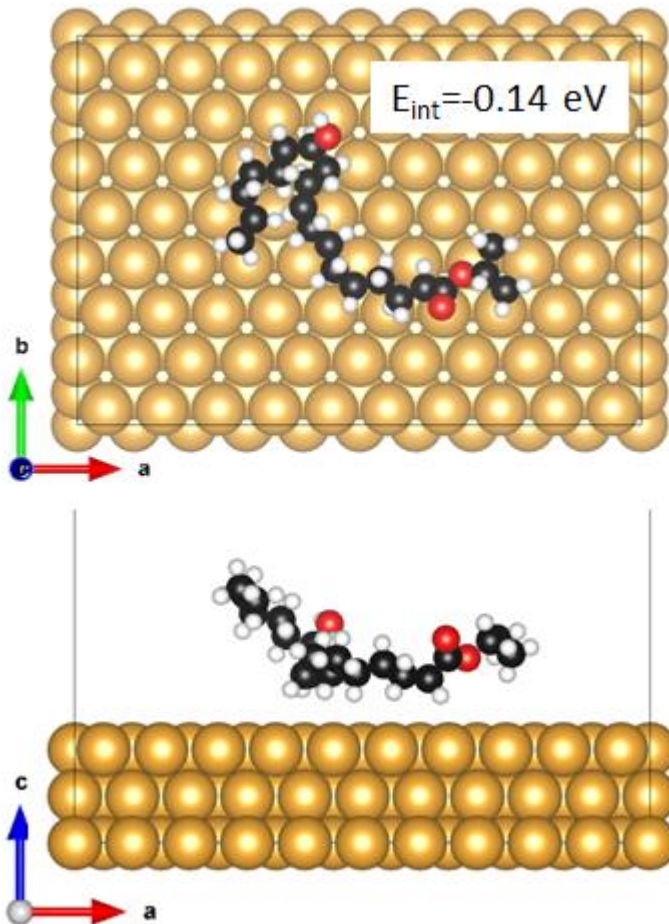


8.1 nm  $\pm$  5.0 nm.  
TEM image 8 months after preparation.

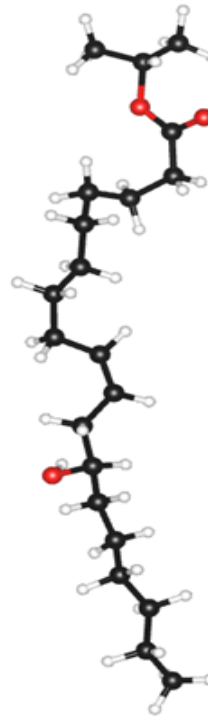
# Stability of nanoparticles in castor oil: Interaction energy calculations

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

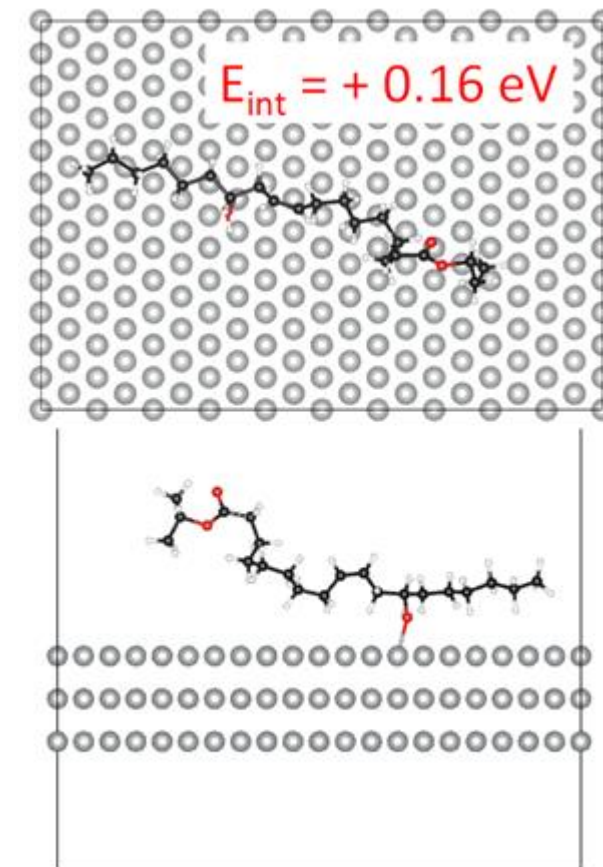
**GOLD**



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:  $(1.8 \pm 0.2) \cdot 10^{-7}$  moles/cm<sup>2</sup> min

Flux HiPIMS:  $(0.9 \pm 0.1) \cdot 10^{-7}$  moles/cm<sup>2</sup> min

$f = 800$  Hz,  $T_{ON,-} = 20$   $\mu$ s,  $I_{pk} = 0.3$  A/cm<sup>2</sup>

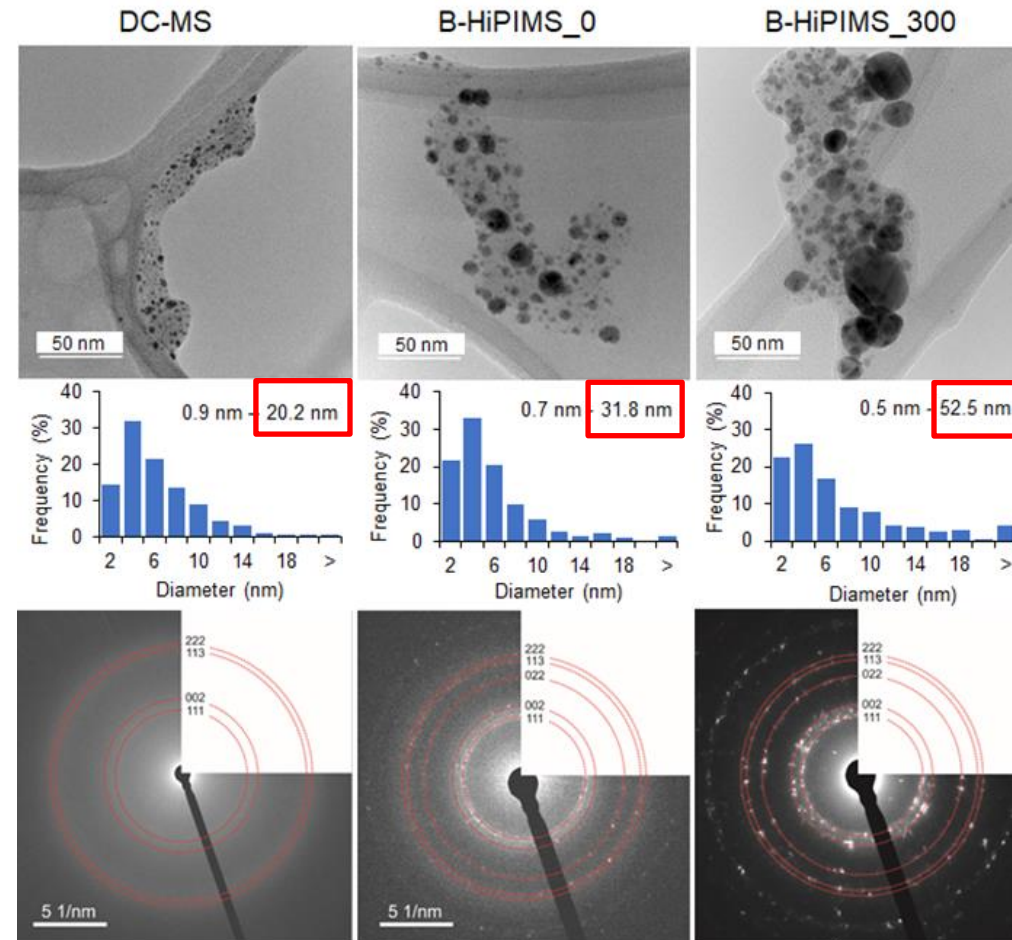
Flux B-HiPIMS:  $(0.2 \pm 0.1) \cdot 10^{-7}$  moles/cm<sup>2</sup> min

$f = 800$  Hz,  $T_{ON,-} = 20$   $\mu$ s,  $I_{pk} = 0.3$  A/cm<sup>2</sup>

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

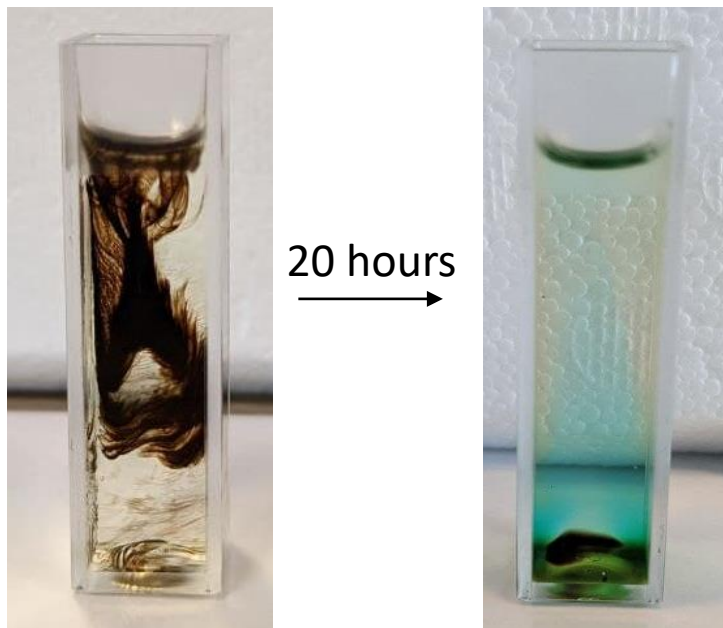
Number of particles larger than 20 nm

- 0.1% for DC-MS,
- 1.3 % for HiPIMS (B-HiPIMS\_0)
- 4.2 % for bipolar HiPIMS (BHIPIMS\_300)

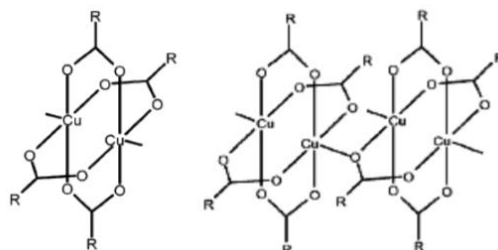
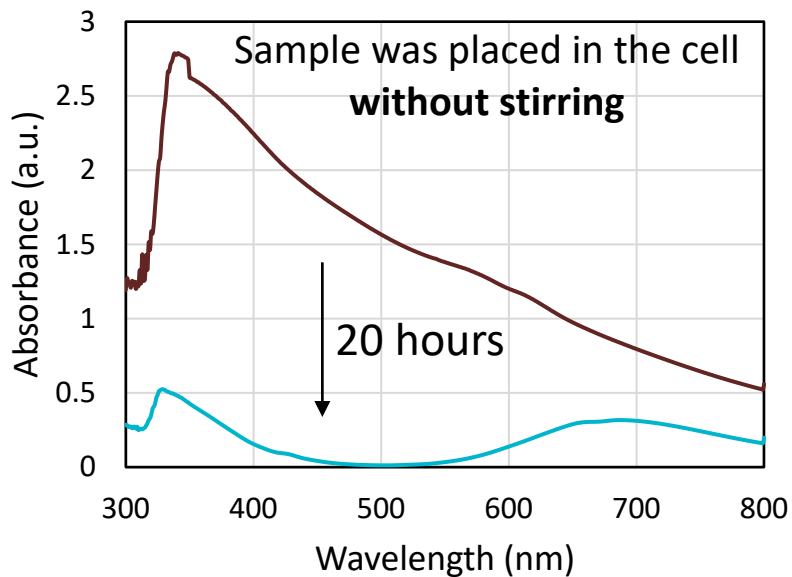
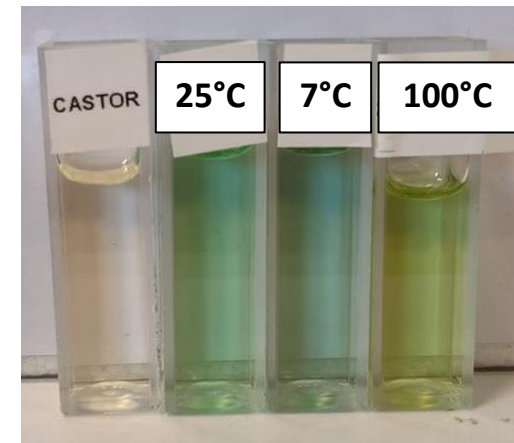
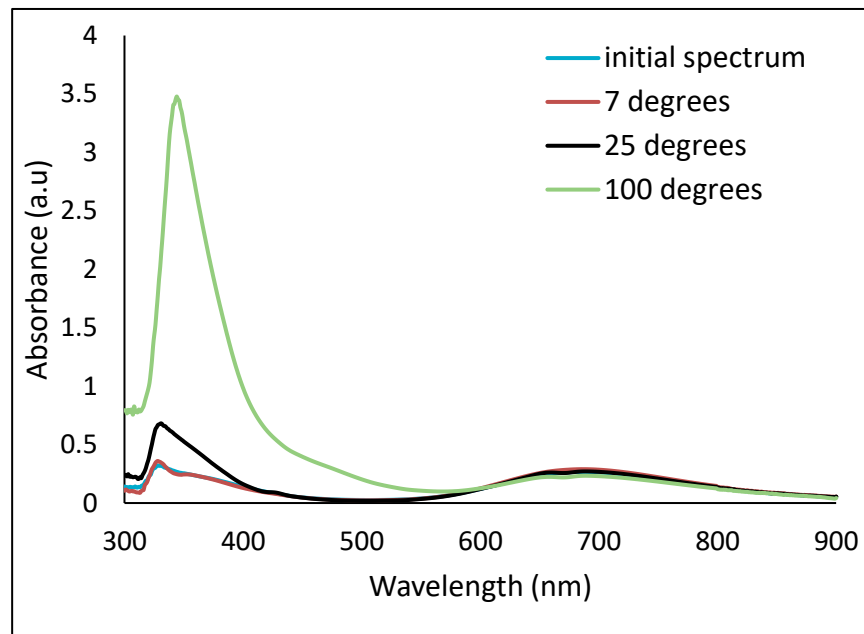


### **3. What if we sputter copper onto castor oil ?**

# Oxidation of Cu-NPs in castor oil

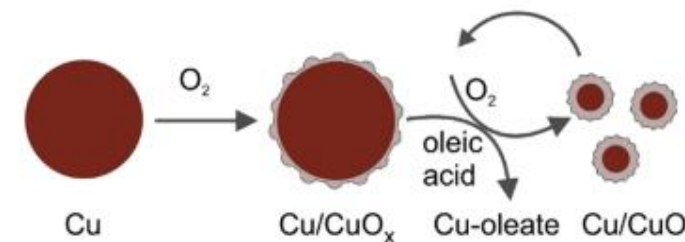


20 hours



Copper (II) oleate  $\longrightarrow$  Cu<sub>2</sub>O 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

