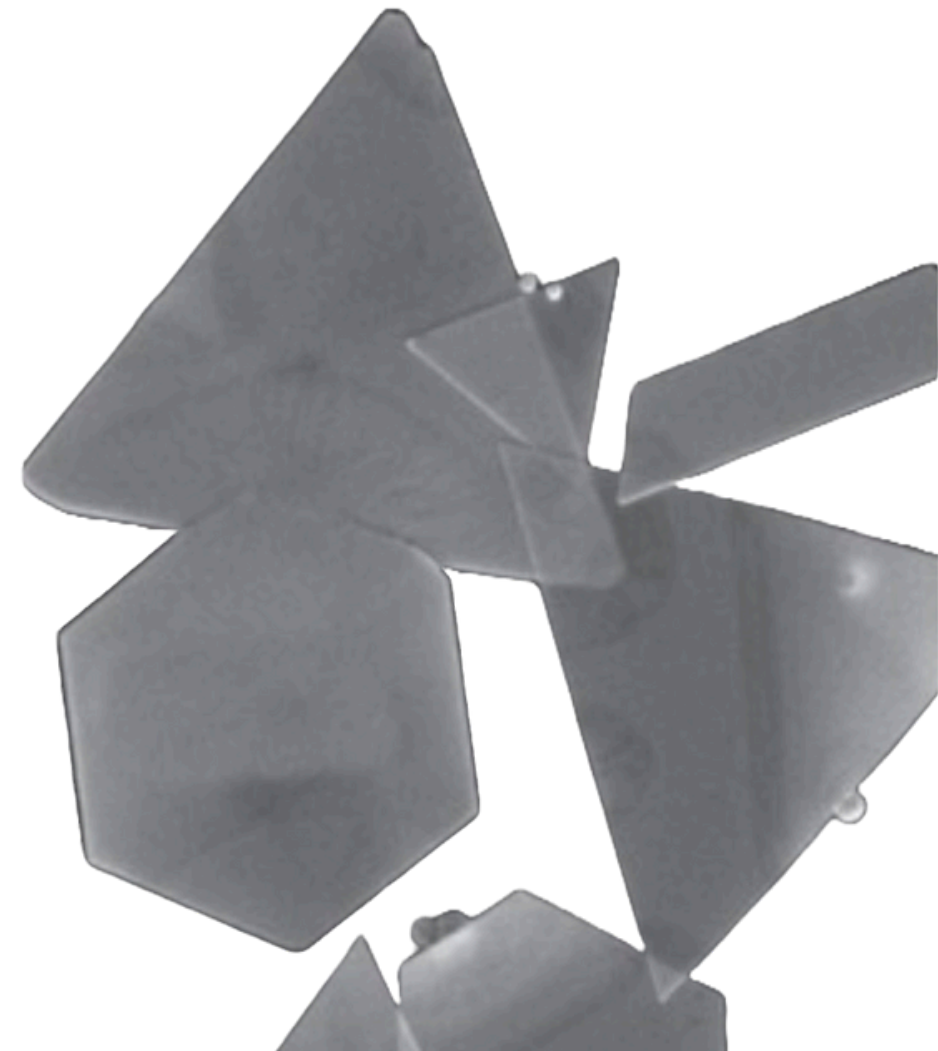


# Nanophotonics & metrology Lab

27/06/2024



*Optimization of  
Ag Micro-flakes  
Fabrication for  
Plasmonics  
Applications*

MEHDI AMOR

# Presentation Map

**1**

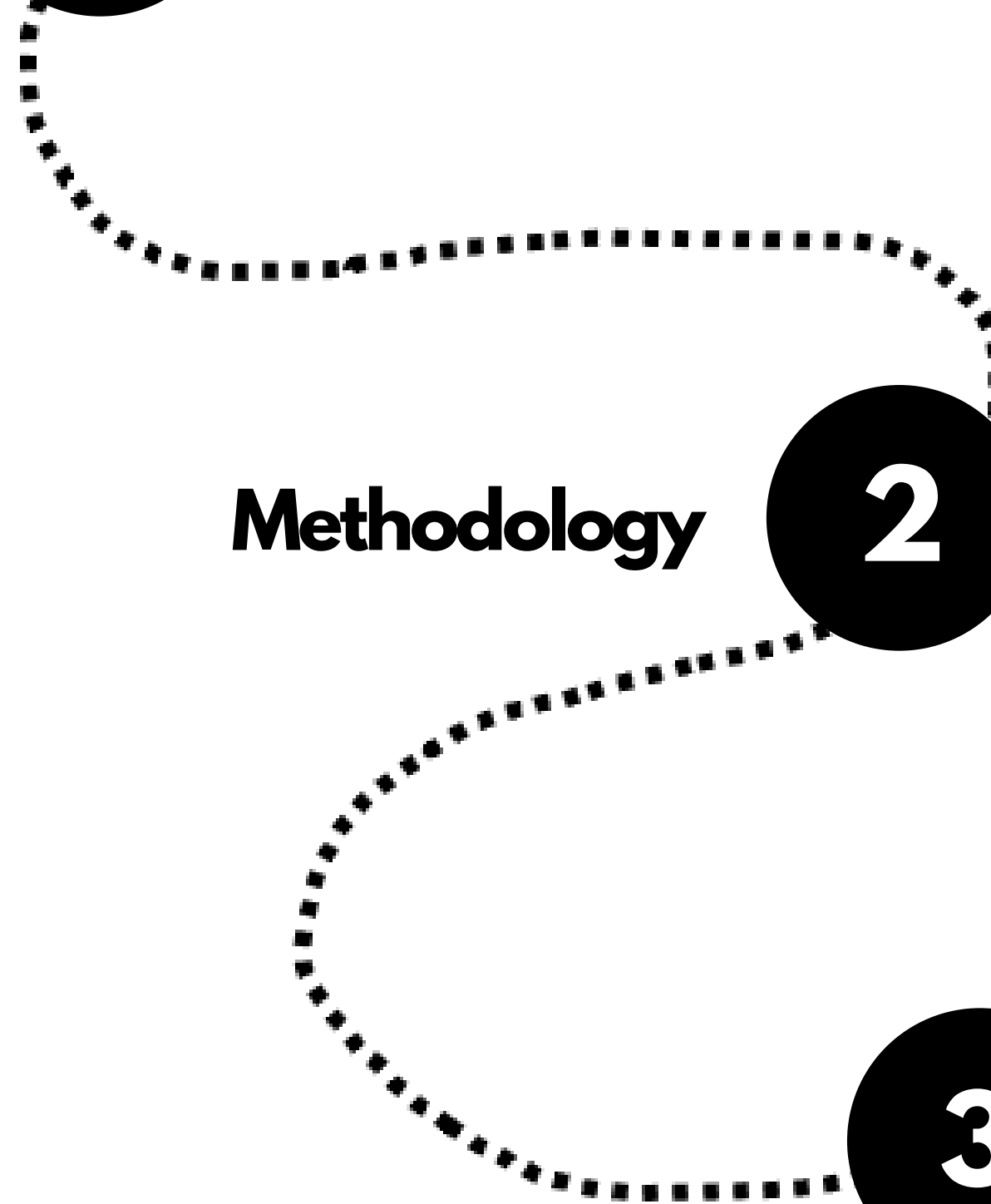
**Introduction and  
Literature Review**

**Methodology**

**2**

**Results**

**3**



# Introduction



**Performance of plasmonic systems hindered by Ohmic losses at optical frequencies**



**Employ crystalline materials that exhibit lower roughness and are free from structural defects**

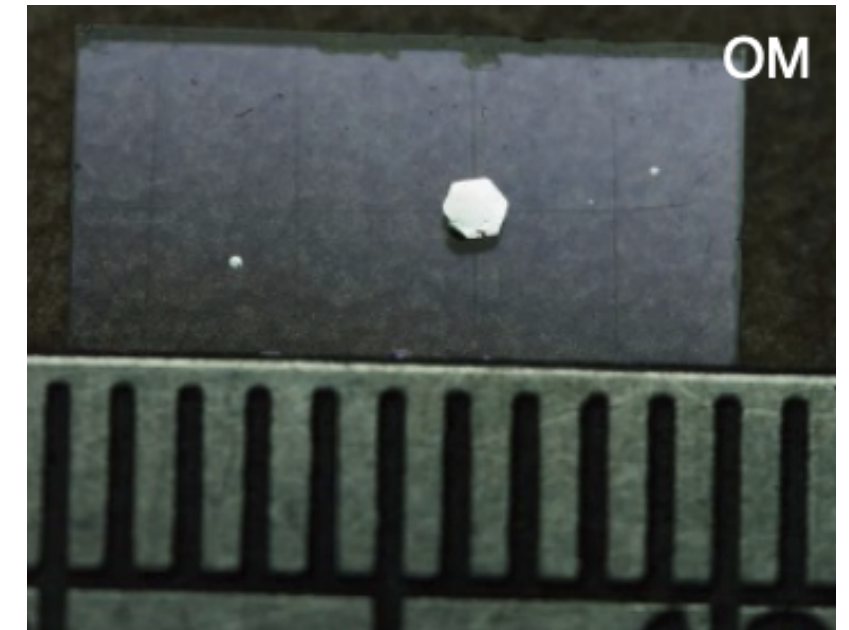
**Familiarizing with colloidal synthesis methods and theory**

**Optimizing synthesis parameters for fabricating silver flakes**

**Sample characterization**

# Literature Review

Wang et al.  
(2015)



*Ammonium hydroxide (NH<sub>4</sub>OH) controlled polyol reduction method*

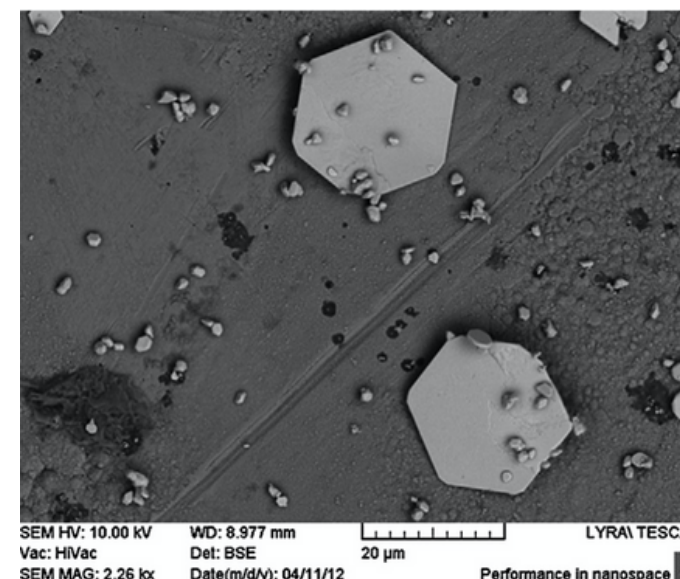
*1 mm diameter, thicknesses of tens of microns*

*SPP propagation lengths exceeding 100 μm in the red wavelength region.*

3



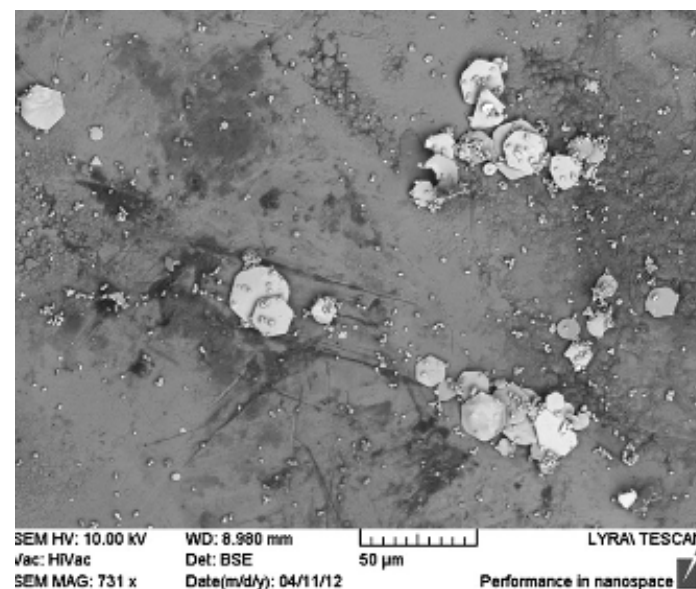
Zhang et al.  
(2019)



*Metol and Silver Nitrite as reactants*

*Thicknesses between 100 and 300 nm*

Lyotov et al. (2014)



*20 - 30 μm diameters*

# Methodology

## Materials, Reagents and Experimental Setup

*Metol and Silver Nitrite*



*Simplicity of the reaction, quick, using primarily two reagents only*



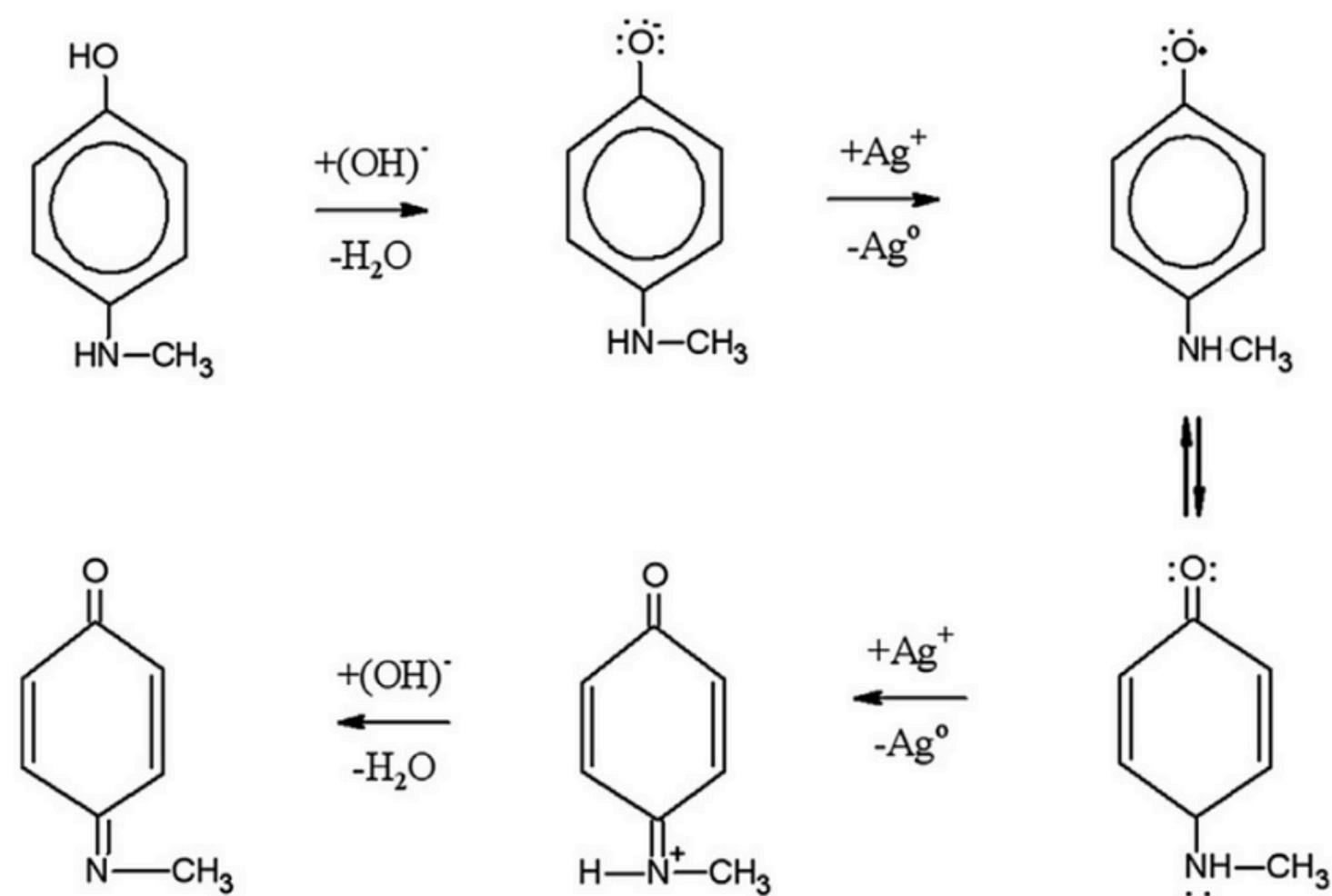
*Easier to conduct optimization experiments and identify what works best*

*Setup*



*Plastic containers, automatic stirrer, hotplate, centrifuge*

# Concise Description of the Reaction Steps



Mechanism of reduction of Silver Nitrate aqueous solution with Metol

# Colloidal Growth Theory

*Why?*



*Cheaper than cleanroom processes*



*Avoids the forming of semicontinuous or grainy thin films*

*High surface ratio areas*

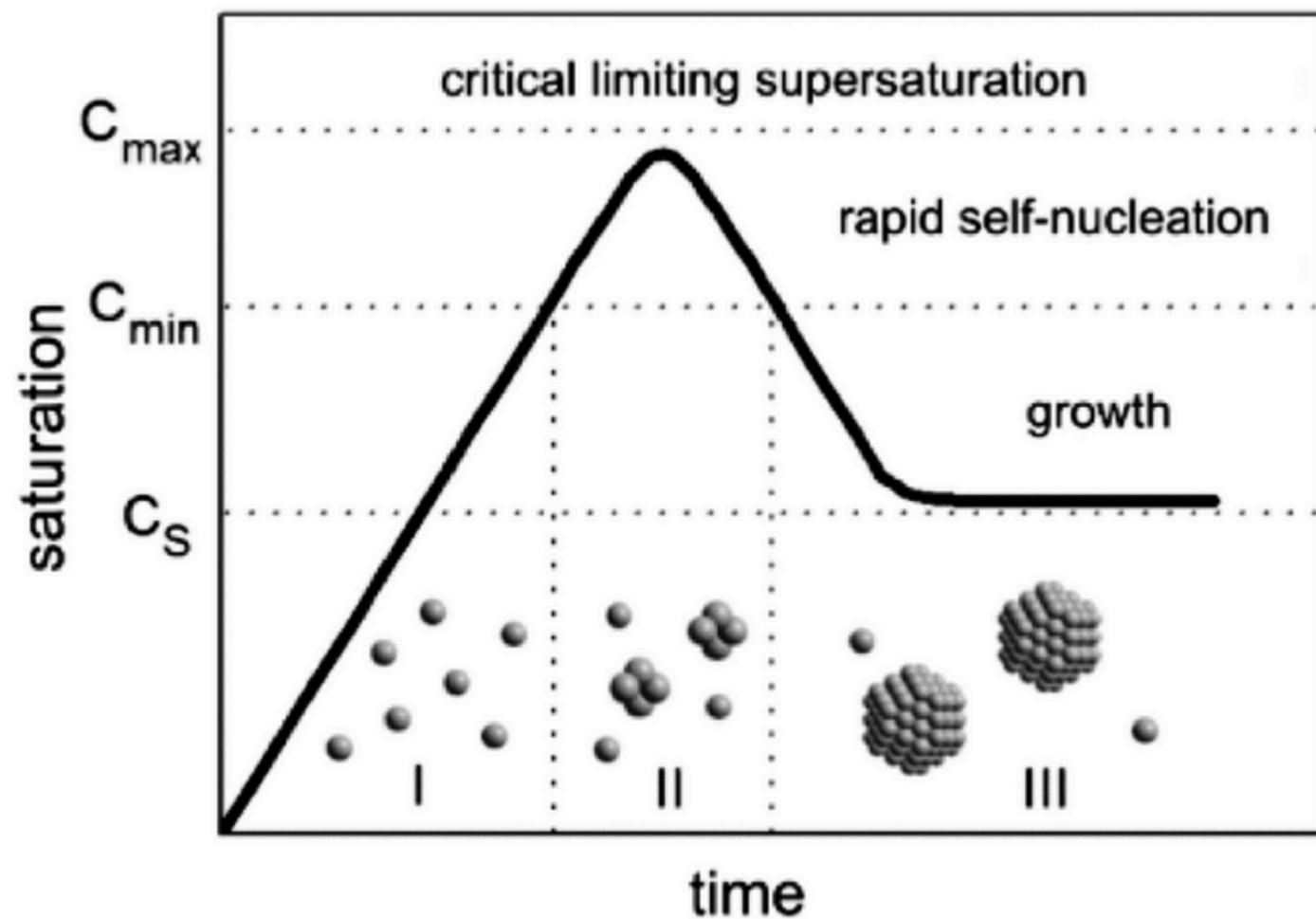
*Classical nucleation theory introduced by LaMer, involves two main stages*

**1**

*Nucleation occurs when  
small, stable nuclei form*

**2**

*Growth occurs when additional  
monomers deposit onto these nuclei*



*Evolution of the monomer concentration vs time according to LaMer's theory of burst nucleation*

**The Gibbs free energy of a spherical cluster can be expressed**

$$\Delta G = -\frac{4}{3}\pi r^3 |\Delta G_V| + 4\pi r^2 \gamma$$



$$r_c = \frac{2\gamma}{|\Delta G_V|}$$

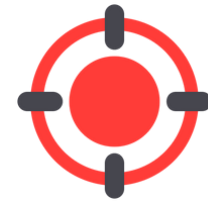
**Below  $R_c$**

*Surface energy is higher, pushing the system toward dissolution*

**Above  $R_c$**

*Volume energy is higher, thus additional atoms will preferentially attach to it*

# Variables Testing



*The chosen experiments aimed to progress from vague optimization to clearer information and direction*

***Basic Variables***



*Concentration, Temperature,  
Reaction Time*

***More complex ones,  
related to colloidal growth***



*Supersaturation Control, Stabilizing  
Agents, Seeded Growth*



## Concentration

*Energize the system by  
modulating collision frequency*

*Inspiration from Lyutov paper  
(2.9mM of Metol and 6mM of AgNO3)*

*0.75mM to 9mM with increments  
of 1.5 mM 10 mg/ 40ml*

***Lower concentrations  
for higher growth rate***



## Temperature

*Energize the system by  
modulating collision frequency  
and molecule energy*

$$k = Ae^{-\frac{E_a}{RT}}$$

*1°C, room temperature  
( 20°C), and 40°C*

***Lower temperatures for  
higher growth rate***



## Reaction Time

*Assess whether more  
reaction leads to  
further growth*

*Direct check and 10  
minutes later*

***Longer reaction time  
allows for more growth***



## **Supersaturation Control**

*Concentration of solute exceeds  
the equilibrium solubility*

*Completing one cycle only*

*Incrementally adding 10  $\mu\text{l}$ , 30  $\mu\text{l}$ , 50  $\mu\text{l}$ , and 100  $\mu\text{l}$  of  
metol, with waiting times of either 1 minute, 3  
minutes, or 5 minutes between each addition*

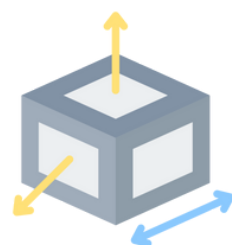


## **Seeded Growth**

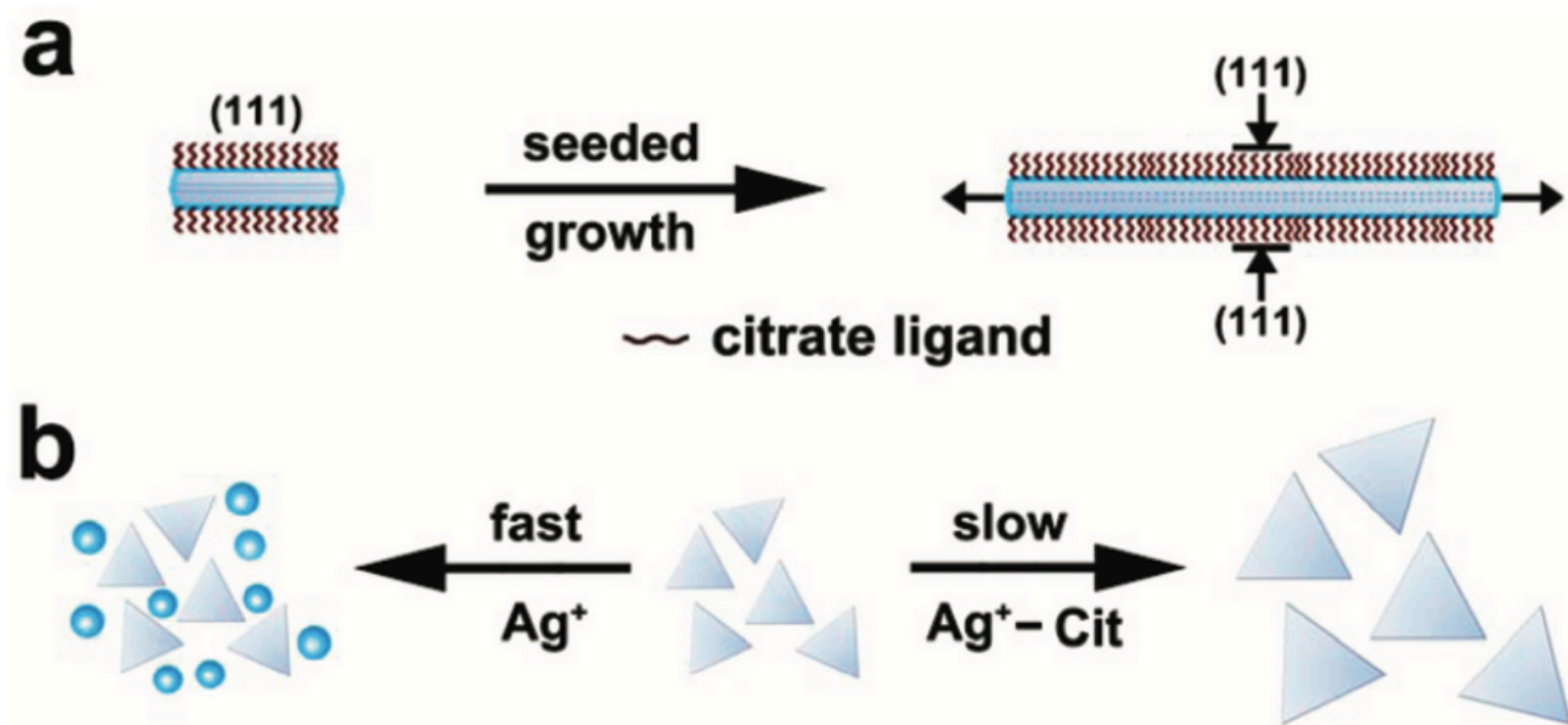
*Separation of nucleation and  
growth phases*

*Surface energy necessary for nucleation is  
lower at phase boundaries*

*Requiring seeds to form relatively slowly to allow  
sufficient time to harvest and use the seeds  
before they grow larger*



# Stabilizing Agents



(a) The citrate ions selectively protect the {111} facets of Ag

(b) Ag - Citrate complexes are used as the precursors, slows down the reaction rate

Commonly used tool in colloidal growth

Serve as capping agents to control the size of spherical particles

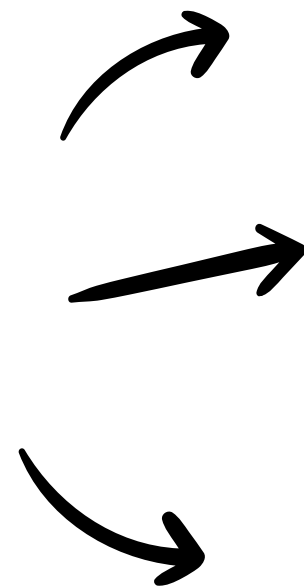
Adsorb onto specific facets of crystalline particles reducing their surface energy

Citrate and Halide ions (KCl)

Ratios of 1:10, 1:100, 1:1000

# Characterization Methods

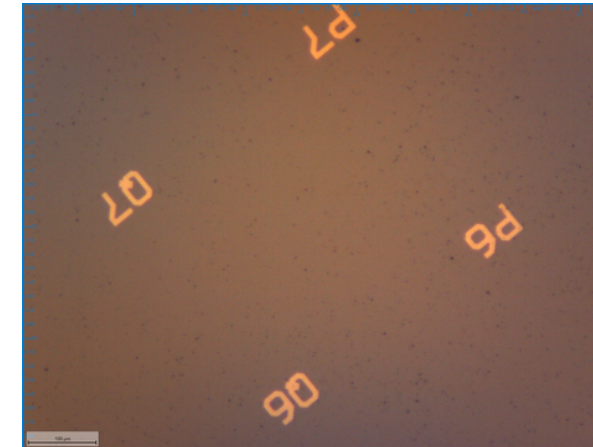
Three features  
can be considered



*Lateral dimensions*

*Surface smoothness*

*Contamination by other  
silver nanoparticles due to  
aggregation*



*Gridded Substrate*

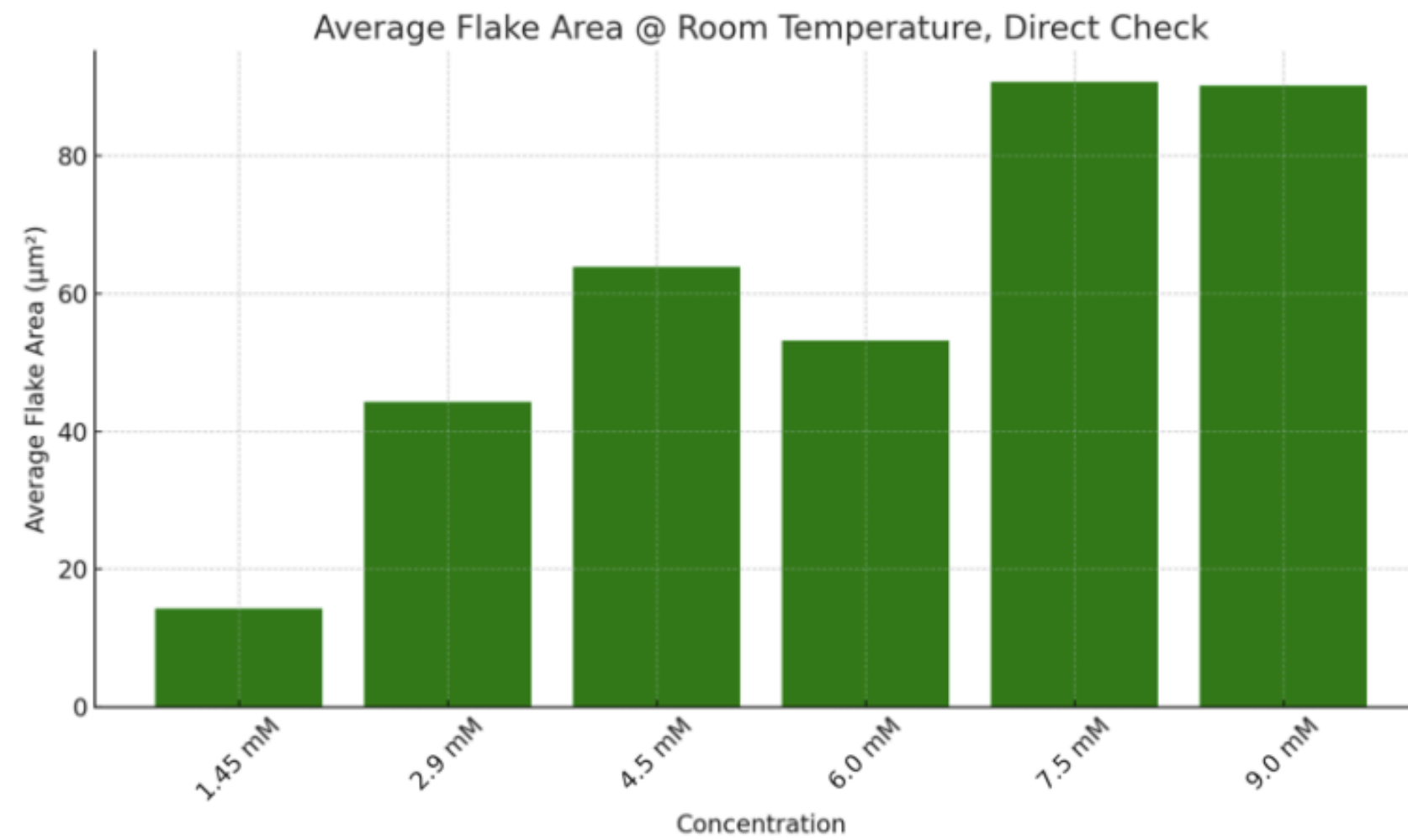


*Optical Microscope*

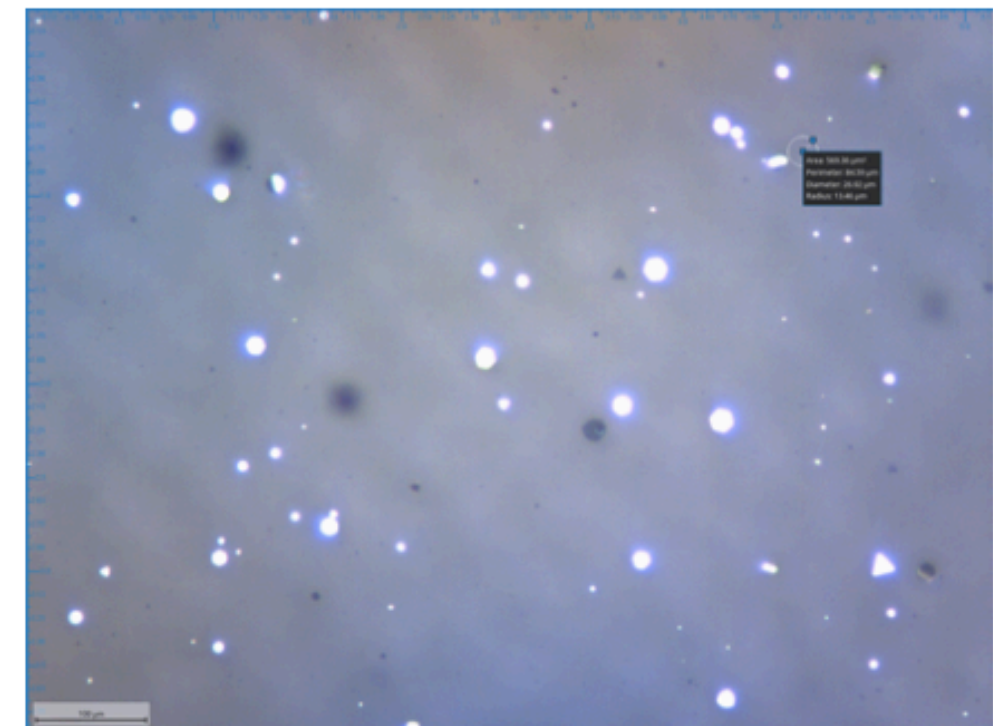
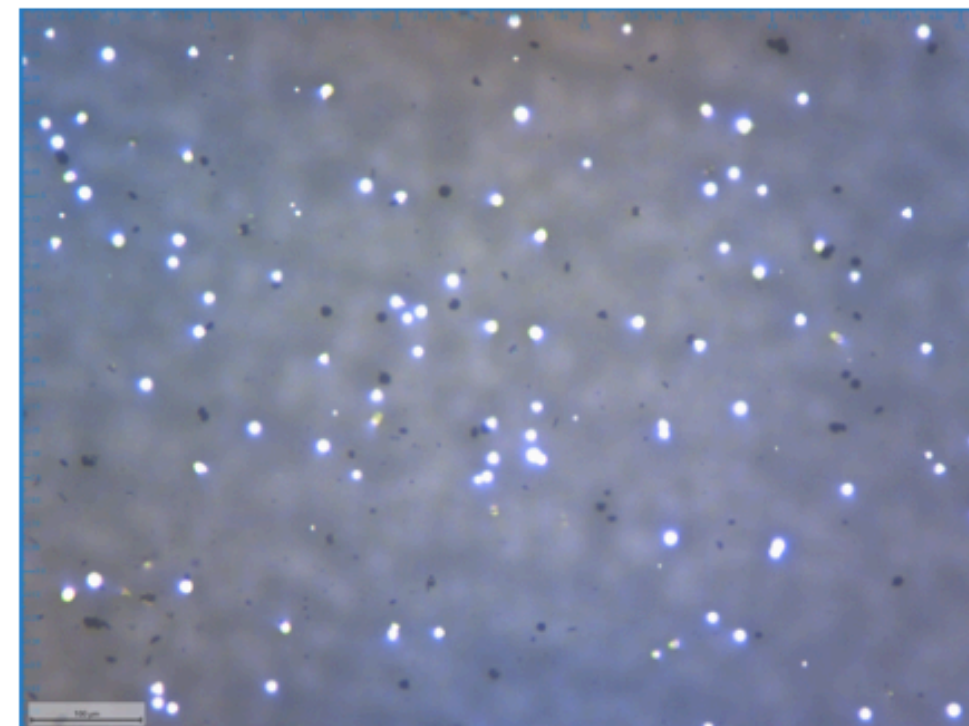


*SEM*

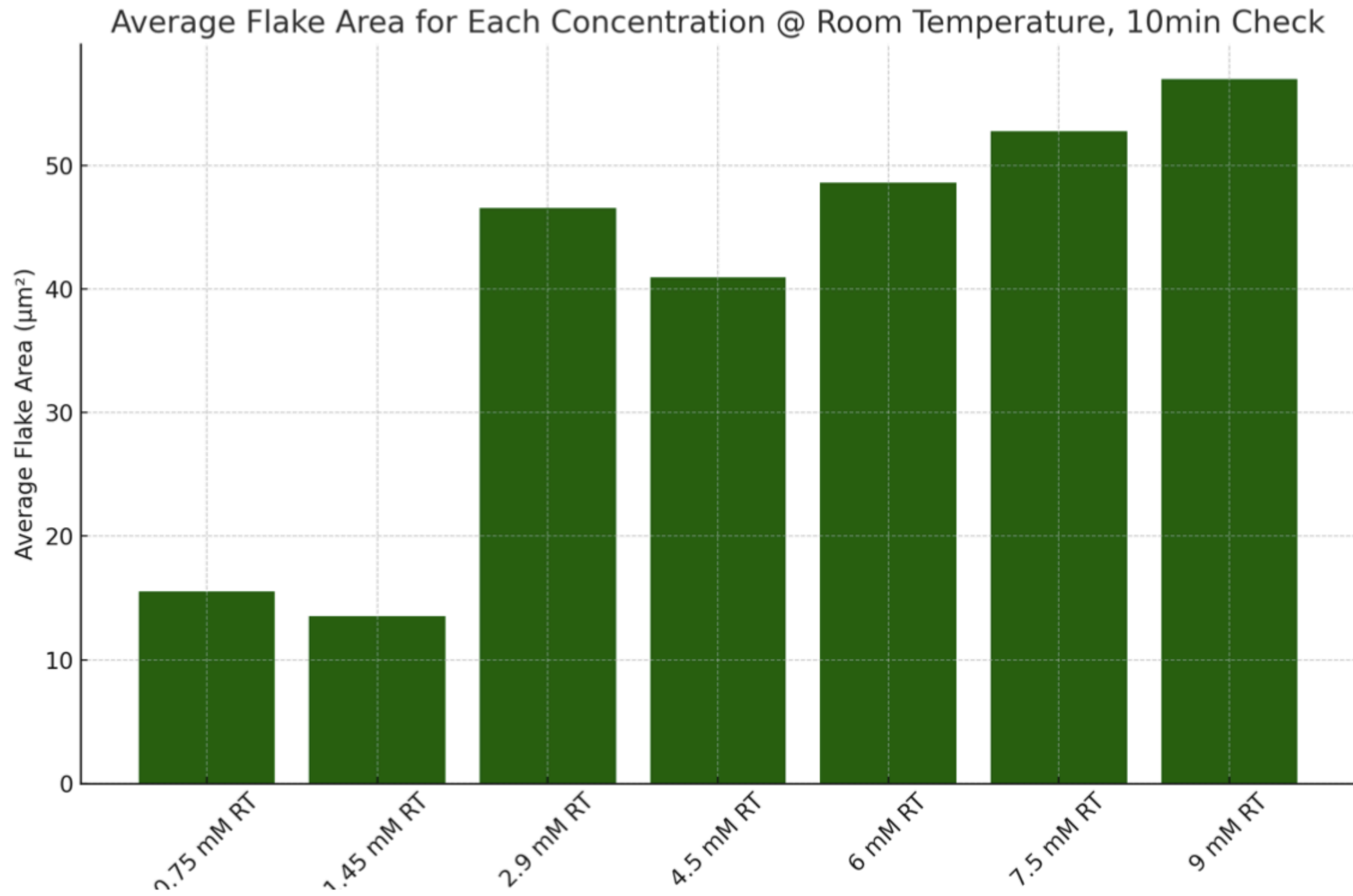
# Results



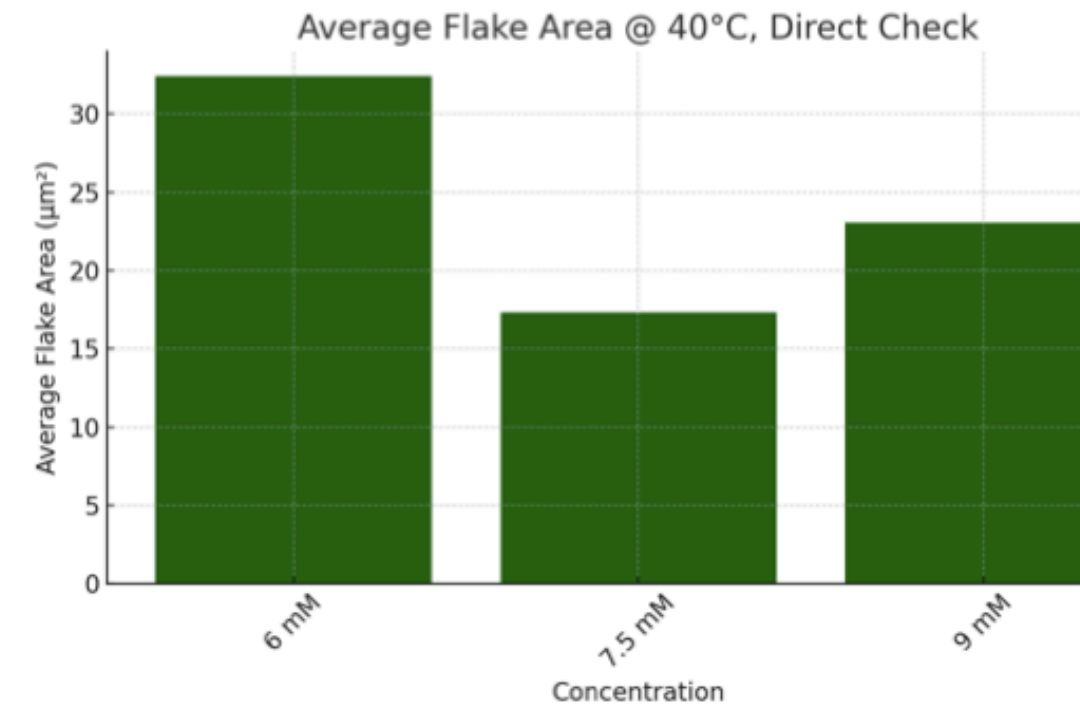
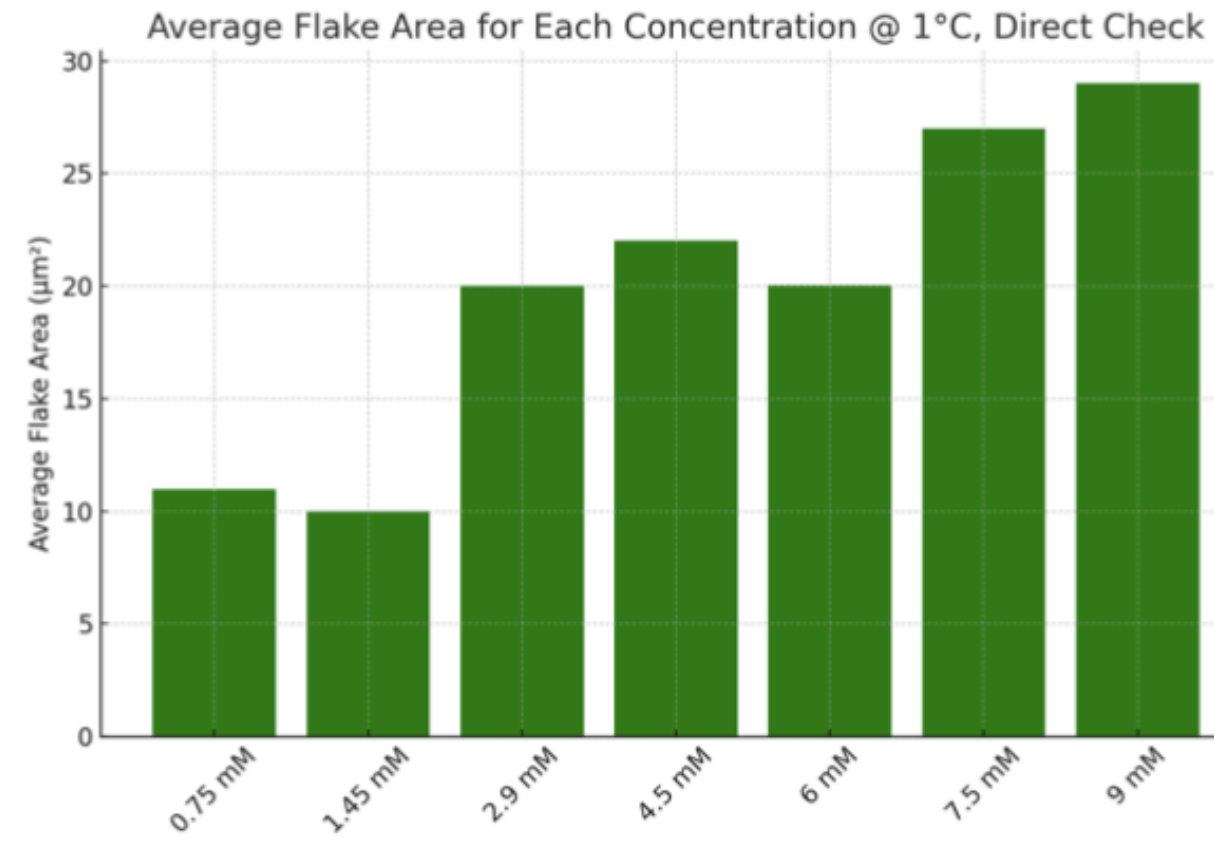
## Concentration



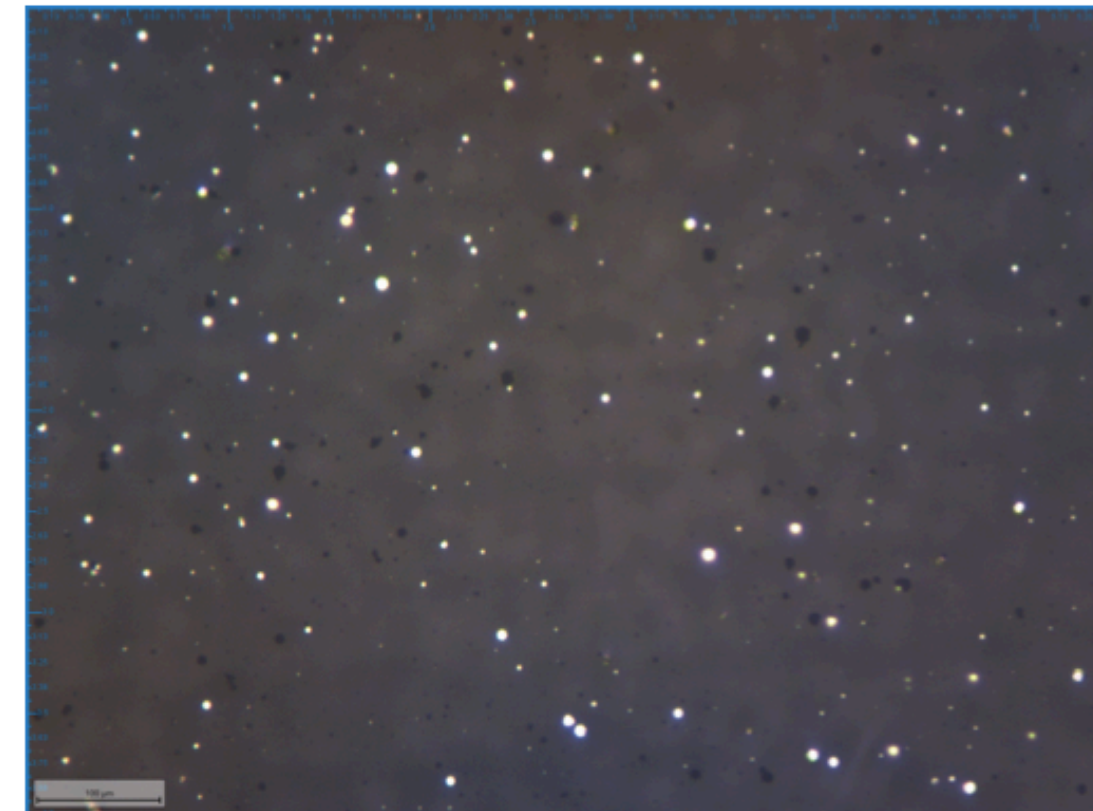
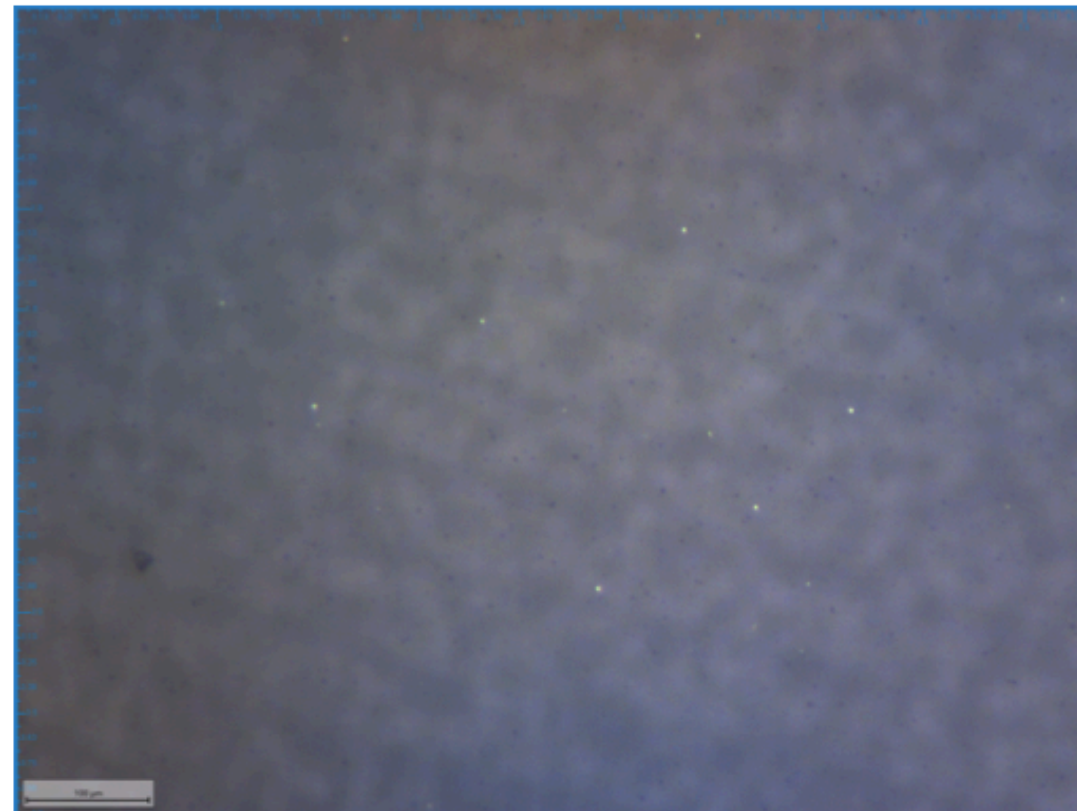
Samples of two solutions (a) 2.9 mM and (b) 9 mM @ Room Temperature, Direct Check



*Reaction  
Time*

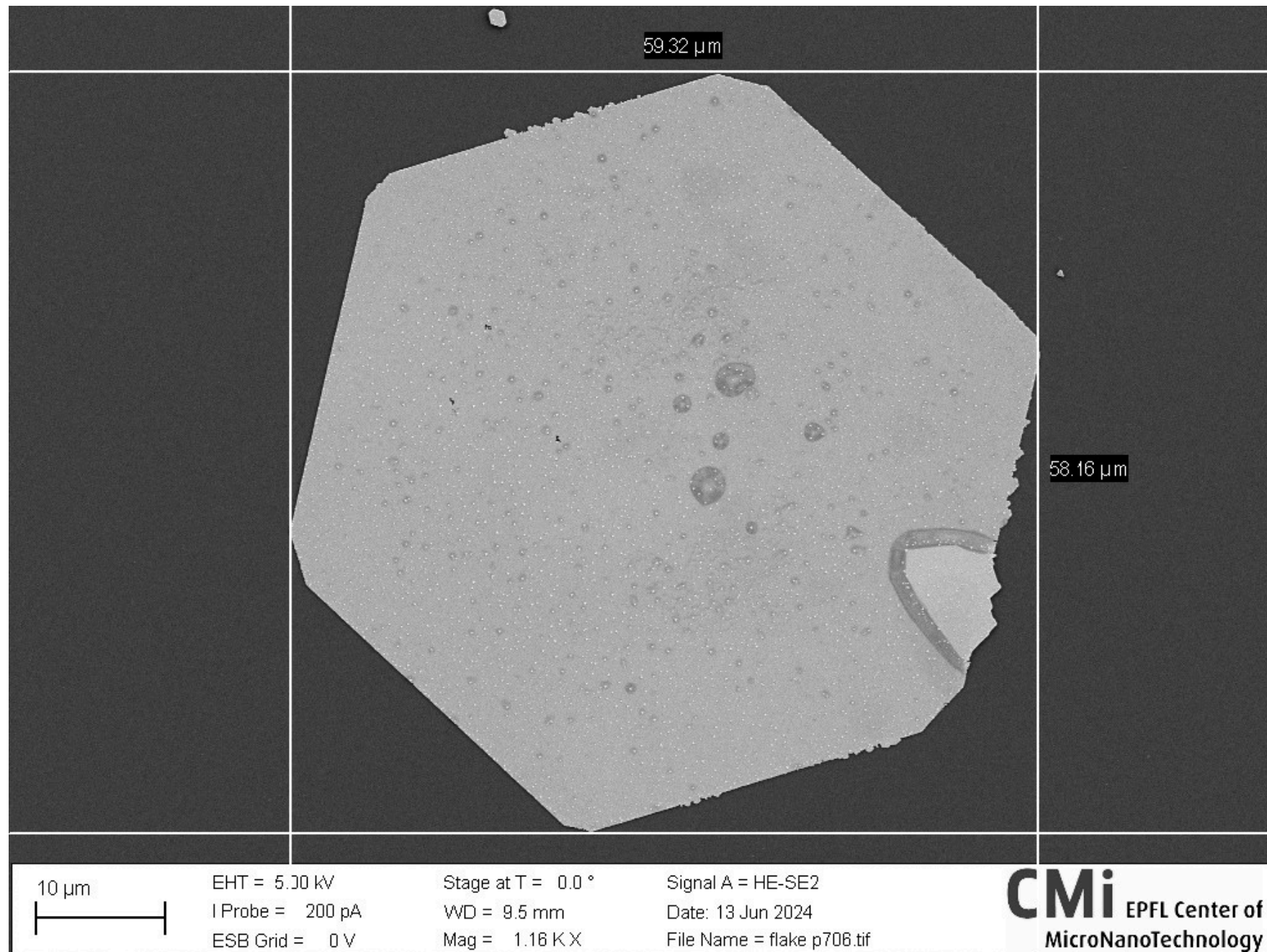


## Temperature

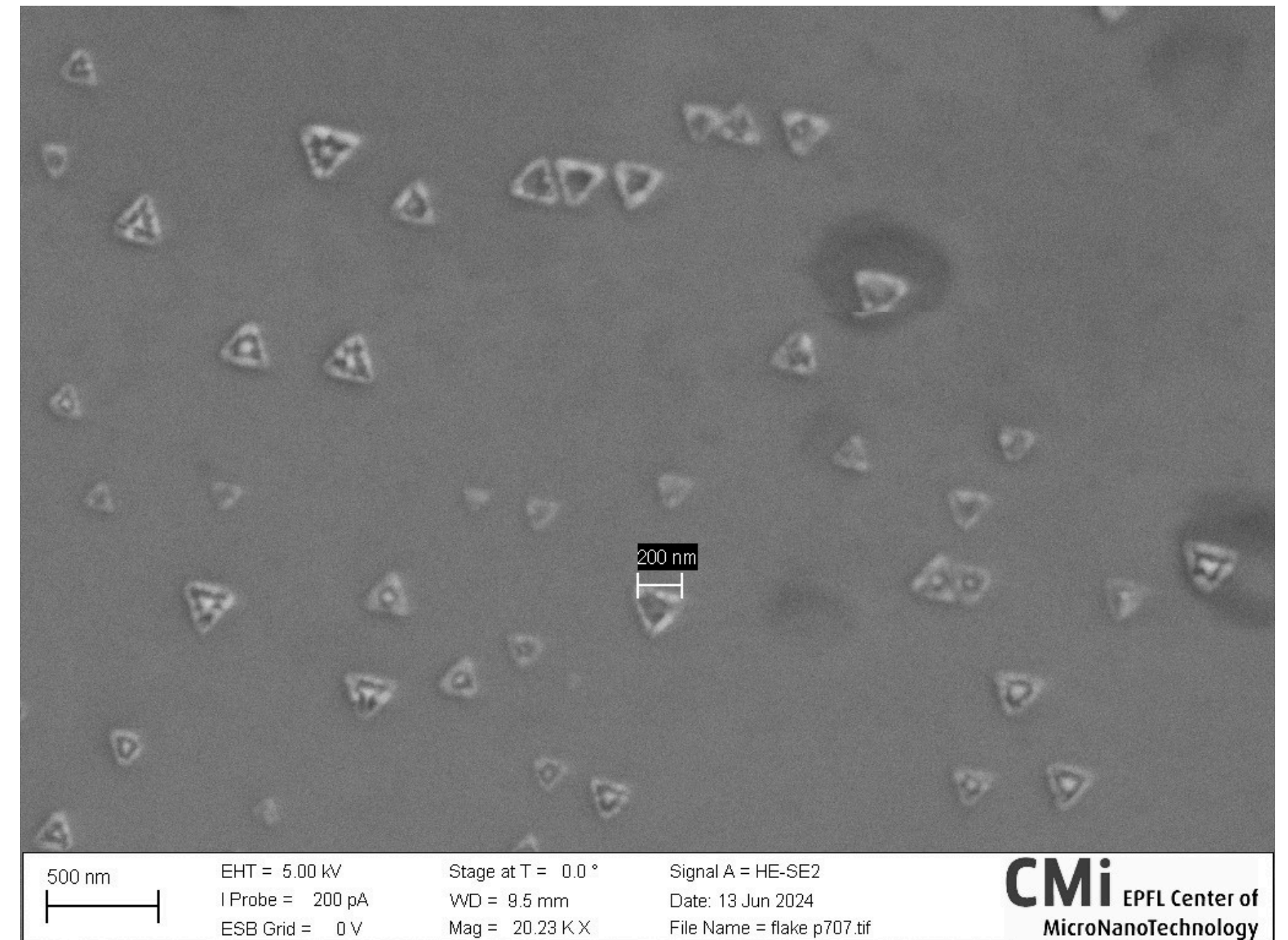


Samples of two solutions (a) 2.9 mM and (b) 9 mM at 1°C, direct check

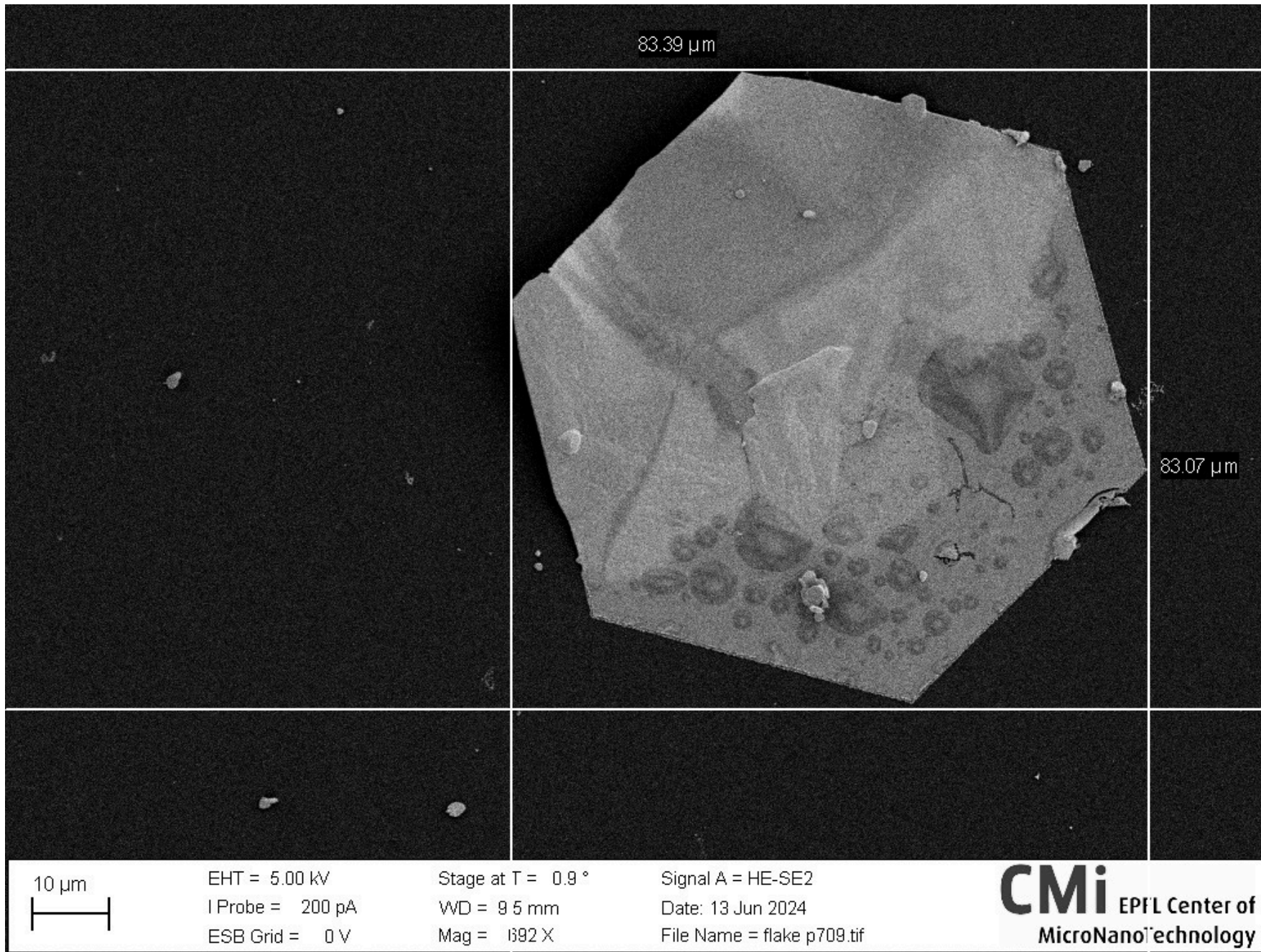
# Supersaturation Control



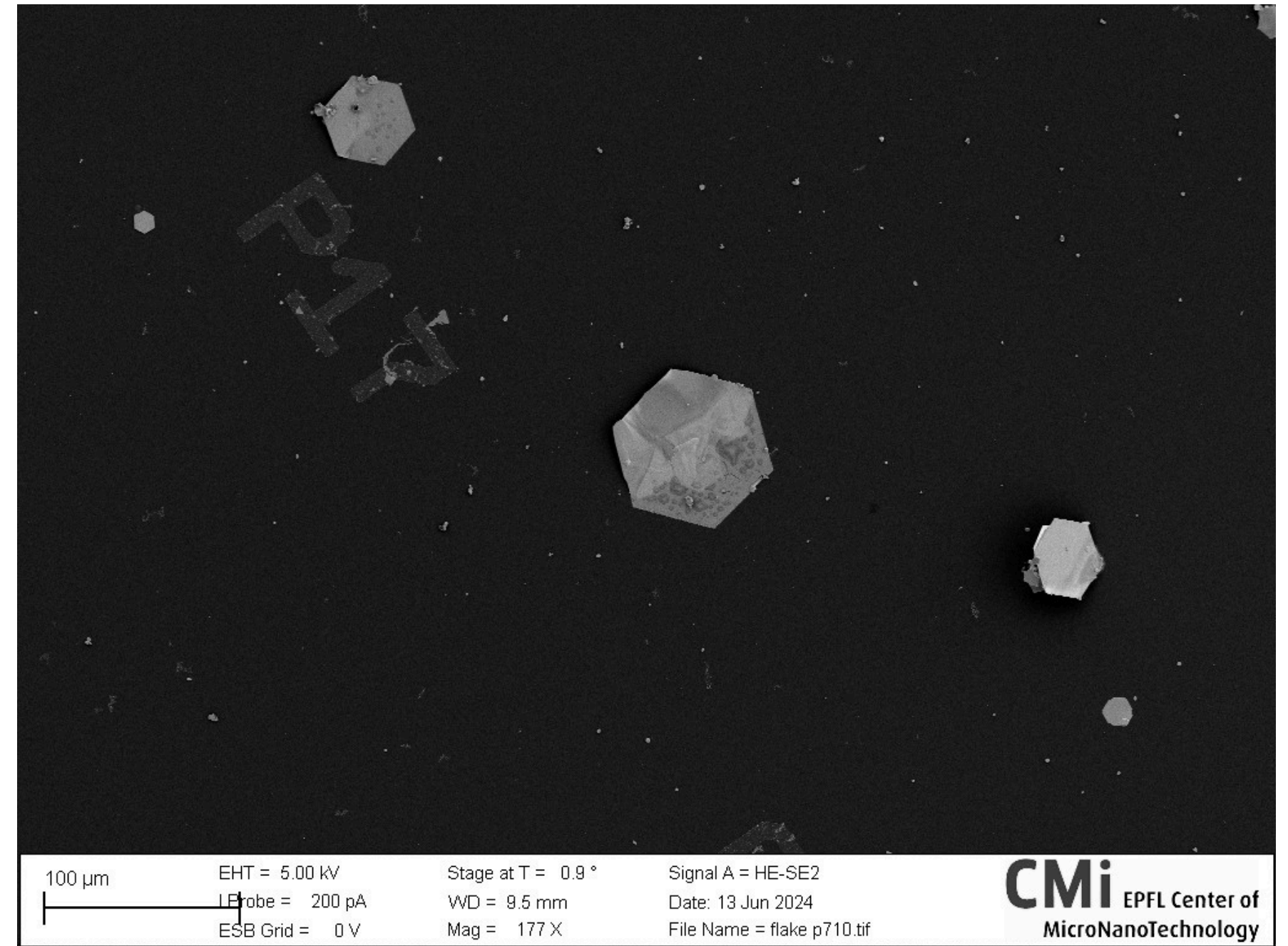
*SEM Image of a 60  $\mu\text{m}$  diameter flake, showing surface imperfections*



*Triangular nanoparticles contamination on the flake's surface*



*SEM Image of an 80 μm diameter flake, showing high surface roughness*



*Top view of the flake on a gridded substrate*

# Stabilizing Agents

**Citrate**

*For 1:10 ratio*

*No flakes appearing at all, probably due to the stabilization of the reaction*

*For 1:100 and 1:1000 ratio*

*Small flakes (-10um diameter)*

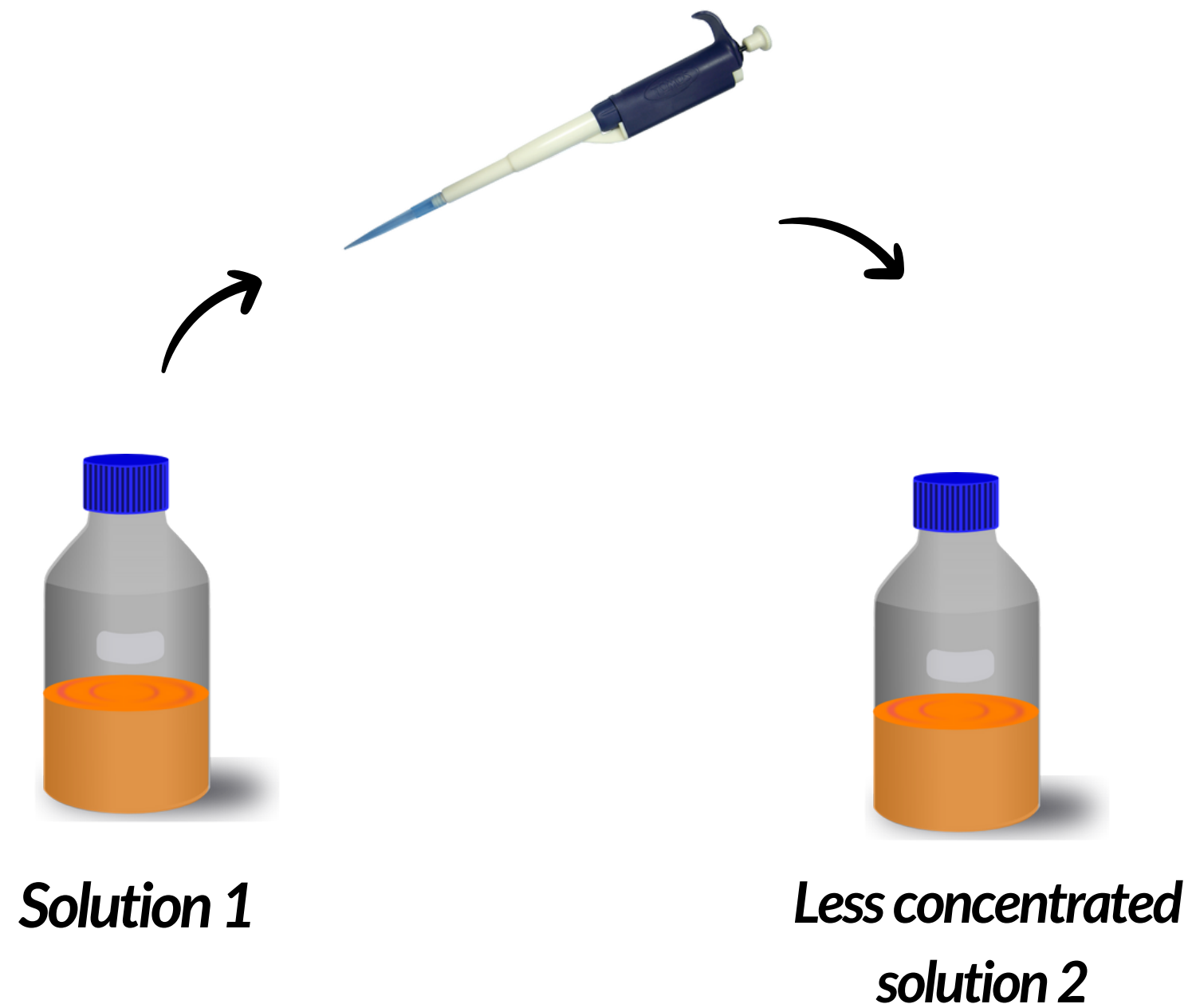
**Potassium Chloride (KCl)**

*30mM, 3mM and 0.3 mM, 0.03mM*

*At the beginning, middle, and end of the process*

*Small flakes also (-10um diameter)*

# Pre-seeded Growth



*Small flakes with lot of aggregation  
(-10um diameter)*

*Compares to  
supersaturation control*

# Conclusion

*Basic Variables*



*Higher initial concentrations facilitates rapid growth, but plateaus. 9 mM is optimal for both reactants*

*Prolonged reactions caused aggregation and settling of the flakes*

*Room temperature was found to be ideal*

*More complex Variables*



*Gradually adding Metal to the AgNO<sub>3</sub> is highly effective in controlling nucleation and promoting growth*

*Citrate and KCl, and seeded growth did not yield significant improvements*

**Thank you  
for listening**