Report

Summer Student: Irene Schiesaro, Università degli Studi Roma3, Italy.

Supervisor: Stephan V. Roth, DESY, Germany. - Wiebke Ohm, DESY, Germany.

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Abstract

Nobel metal nanoparticles (NPs), especially silver and gold, have attracted great attention due to their innumerable applications in catalysis, photonics, Surface Enhanced Raman Scattering (SERS) and in the medicinal field.
The aim of this work is to conduct a first study on the nanoparticles formation from silver nitrate ($AgNO_3$) with the airbrush spray deposition technique: a fast, economic and reproducible method for coating surfaces.
A qualitative and quantitative study of samples obtained from various concentration of $AgNO_3$ solution was done with the Atomic Force Microscope AFM in order to correlate the nanoparticle arrangment and size to spray parameters.
This will allow studies focused on in-situ and in-operando GISAXS investigations with microfocussed synchrotron radiation during spray deposition with the final purpose of following the nanostructural evolution in real-time and correlate nanoscale morphologies with optoelectronic properties.

Contents

1 Introduction

Nanotechnology refers to the branch of science and engineering dedicated to materials having dimensions from about 1 to 1000 nanometers.
At this scale the materials properties change significantly from those at larger scales and quantum effects rule the behavior and properties of particles (melting point, fluorescence, electrical conductivity, magnetic permeability, and chemical reactivity) that change as a function of the size. [1]
Nobel metal nanoparticles (NPs), especially silver and gold, have attracted great attention due to their innumerable applications in catalysis, photonics, Surface Enhanced Raman Scattering (SERS) and in the medicinal field. [2]
There has been an extraordinary growth in nanoscience and technology in recent years, mainly due to both the development of new techniques to synthesize nanomaterials and the accessibility of tools for the classification and manipulation of nanoparticles.
The aim of this work is to conduct a first study on the nanoparticles formation from silver nitrate ($AgNO_3$) with the airbrush spray deposition technique, in order to control their shape and size. This will allow future studies focused on in-situ and in-operando GISAXS investigations with microfocussed synchrotron radiation during spray deposition with the final purpose of following the nanostructural evolution in real-time and correlate nanoscale morphologies with optoelectronic properties.

2 The AFM technique:

Samples were analyzed with the atomic force microscope (AFM), a kind of scanning probe microscopes (SPM) that allow to obtain images from a wide variety of samples at extremely high (nanometer order) resolution.[3]
It is composed of:

- A probe formed by a silicon or silicon nitride cantilever with a sharp tip which scan along the sample surface.
- An optical system control: the forces (Van der Waals) acting between the tip and the sample cause a deflection of the cantilever, measured by using a laser spot reflected from the top of the cantilever towards a photodiode.
- A piezoelectric scanner that facilitate tiny but accurate and precise movements and an electronic feedback loop employed to keep the probe-sample force constant during scanning.

The combination of these elements, managed by a special software, allow the AFM to generate an accurate topographic map of the surface features.
The AFM used was the Probe Nanolaboratory NTEGRA instrument from NT-MDT.
The software used to analyze images was WSxM (WSxMv 5.0, developed by Horcas et al.) [4]

3 Sample Preparation

In this chapter the cleaning procedure, the preparation of solution and the spray deposition techinque will be discussed. As regards the spray deposition method, the experimental set-up and the spray parameters will be also explained.

3.1 Silicon Substrate Cleaning:

Silicon wafer pieces were cleaned using two different processes:

- Organic cleaning: The silicon substrates were cleaned using in this order: acetone, isopropanol and distilled water. For each substance the substrate was placed in ultrasonic bath for 5 minutes and finally dried with N_2 gas.
- Acid Cleaning: The silicon substrates were placed at first in acetone using ultrasonic bath for 10 min. Then rinsed with acetone, isopropanole, methanol and distillated water. Finally they were placed in an acid bath at 80 °C for 15 min: the acid solution (called Piranha solution) consisted of 130 ml of deionized water (H_2O), 70 ml of hydrogen peroxide (H_2O_2) and 200 ml of sulfuric acid (H_2SO_4).

In order to choose the best cleaning process it was made a comparison between samples prepared in the same spray conditions, just varying the cleaning procedure. (Figure 1). The concentration of $AgNO_3$ solution is 75 mM/l. (Section 3.2).
Piranha solution is a strong oxidizing agent that make the surface highly hydrophilic. [5]. The AFM analysis shows (Figure 1) in fact that acid cleaning results in a more uniform particle shape and distribution than the organic cleaning.

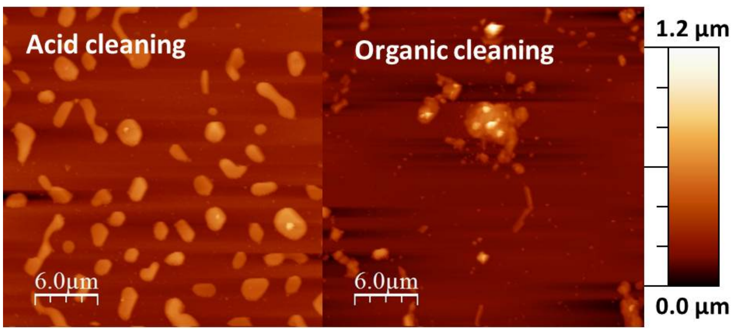


Figure 1: AFM image of nanoparticles obtained by airbrush spray deposition from a $75mM/l$ $AgNO_3$ solution. The substrate temperature was 120 °C. The pressure was 1.5 bar. The sprayed was executed in one single cycle of 10 s at a distance nozzle to substrate of $D = 15cm$.
The image shows the comparison between samples made with acid cleaning and organic cleaning.

3.2 Preparation of solution

The molecular mass of $AgNO_3$ is 168.97 g/mol. It was dissolved in 10 ml ethanol and there were prepared solution of different concentrations from 5 to 100 mM/l.
The mixture of ethanol and $AgNO_3$ was placed in ultrasonic bath to dissolve $AgNO_3$ powder and the solution was finally pressed throught a $0.4\mu m$ syringe filter to eliminate large particles.

3.3 Spray deposition technique

Samples were made using the spray deposition technique: it is a fast, economic and reproducible method for coating surfaces. It consist of the atomization of the spray solution in an aereosol, that is sprayed on the substrate surface where the solvent finally evaporates.
The atomization is done with pressurized gas ($N2$) which is connected to the spray gun. A little part of the solution may eventually evaporate during the trasportation from the nozzle to the sample, the remaining is sprayed by defining a cone in which the sample is located.
When the solution hit the substrate, many processes occurr influencing its distributions on the sample. It is located on a hot plate that allow a faster evaporation of the solution.

3.3.1 Experimental setup

The spray deposition set-up consists mainly of the following parts (Figure 2):

- Spray gun
- Liquid feeding unit
- Temperature control unit of the substrate
- Funcion generator,used for varying the spray time
- Pneumatic switch to trigger the spray.

The spray gun (Harder e Steenbeck GmbH eCo.KG., Germany) used was the GRAFO T3 model with nozzle diameter of 0.4 mm.

3.3.2 Spray parameters for experiments

In Figure 3 a summary of the parameters involved in the sample preparation can be seen. The spray deposition allows to vary the spray time, the pressure, the temperature and the distance nozzle to substrate. The spray time, the temperature and the distance were kept constant at: time = $10s$, Temperature = 120 °C and Distance = $15cm$. The pressure and the solution were varied.

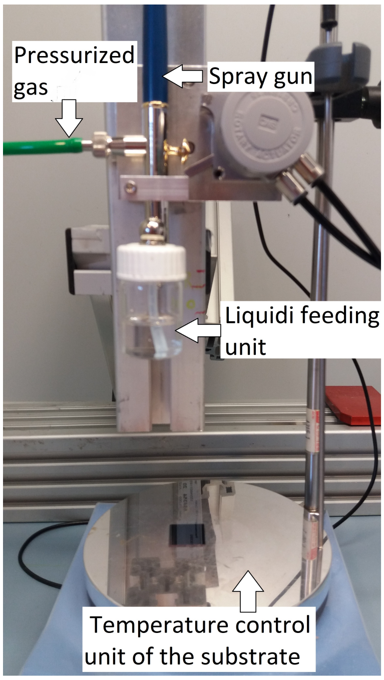


Figure 2: The image shows the spray deposition set-up.

4 Analysis of the spray system

The spray deposition involves a lot of parameters like gas pressure, nozzle to substrate distance, spray time, drying temperature and composition of solution, that can affect sample structure. Thus an analysis of the spray system is important to understand how the nanoparticle growth can be varied.
In this study, the spray amount and the sprayed solution cone diametre were analyzed changing the pressure and the solvent.

At first, it was measured the spray amount and the mean cone diameter of the sprayed solution onto the substrate varying the pressure.
The spray amount measurement was performed using as liquid feeding unit a plastic tube (inner diametre = 4 mm) filled with ethanol and collecting the heights of the liquid inside the tube before and after spraying.
The spraying was executed in one single cycle of 10 s and the pressure was varied from 1.5 to 4 bar. To improve the statistics the heights 5 of different spray cycles were collected for each applied pressure.
The diametre measurement was performed using a tissue and measuring with a ruler the diameter of the circle created by the sprayed ethanol solution.
The spraying was executed in one single cycle of 10 s, the pressure was varied from 1.5 to 4 bar and the distanze nozzle to substrate was 15 cm.
The smallest measurement that was possible with the ruler was 0.1 cm.

SPRAY AMOUNT MEASUREMENTS		
Time (s)	Solvents	Pressure (bar)
10	Ethanol	1,15
		1,6
		2
		2,5
		3
		3,5
		4
10	Distillated Water	1,6
	25%Ethanol	
	50%Ethanol	
	75%Ethanol	
	100%Ethanol	
10	Distillated Water	4,1
	25%Ethanol	
	50%Ethanol	
	75%Ethanol	
	100%Ethanol	

DIAMETRE MEASUREMENTS			
Time (s)	Solvents	Pressure (bar)	Distance (cm)
10	Ethanol	1,15	15
		1,6	
		2	
		2,5	
		3	
		3,5	
		4	
10	Distillated Water	1,6	
	25%Ethanol		
	50%Ethanol		
	75%Ethanol		
	100%Ethanol		
10	Distillated Water	4,1	
	25%Ethanol		
	50%Ethanol		
	75%Ethanol		
	100%Ethanol		

NP SAMPLES				
Time (s)	Concentration of solution (Mm/l)	Pressure (bar)	Distance (cm)	Temperature (ºC)
10	100	1,6	15	120
	75			
	50			
	30			
	25			
	20			
	10			
	5			

Figure 3: The tables show the parameters involved in the experiments.

The error on the diametre was assumed to be 0.5 cm.

The second experiment was done measuring the spray amount and the mean cone diameter of the sprayed solution onto the substrate varying the sprayed solution, increasing the percentage of ethanol in distillated water from 0% to 100%. The spray amount and the diametre were measured at high pressure (P = 4.1 bar) and low pressure (P = 1.6 bar).
Also for this experiment the spray amount measurement was performed using as liquid feeding unit a plastic tube (inner diametre = 4 mm) filled with the solution and collecting the heights of the liquid inside the tube before and after spraying.
The spraying was executed in one single cycle of 10 s. To improve the statistics the heights of 5 different spray cycles were collected for each solvent.
The diametre measurement was performed using a tissue and measuring with a ruler

the diameter of the circle created by the sprayed solution.
The spraying was executed in one single cycle of 10 s and the distanze nozzle to substrate was 15 cm.

4.1 Results obtained from the experiment made by varying the pressure

A linear fit on both spray amount and diametre data was done, that present approximately the same trend (Figure 5). The error on the spray amount was the standard deviation.
From these results useful information for samples preparation can be obtained. High pressures can be used to have a greater amount of sprayed solution, and in this case the cone diameter within the solution is sprayed will be even greater. Low pressure can be used to have a smaller amount of sprayed solution in a smaller cone.
The spray amount per cm^2 was calculated from data, to verify if the trend was approximately constant. Results are in Figure 8. The fit presents a negative slope of order 10^2
The errors on spray amount per cm^2 data were obtained with the propagation of errors formula:
$\sigma_{f(x,y)} = \sqrt{(\frac{\partial f}{\partial x})^2 \cdot (\sigma_x)^2 + (\frac{\partial f}{\partial y})^2 \cdot (\sigma_x)^2}$

4.2 Results obtained from the experiment made by varying the solvents

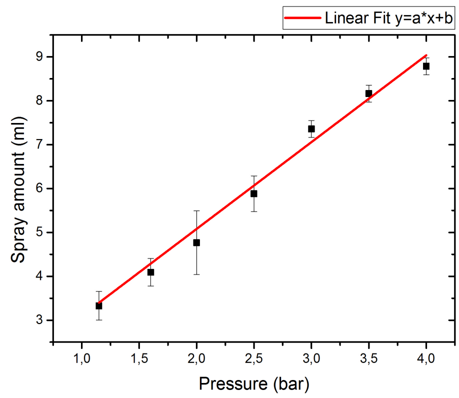
The spray amount data have an unexpected parabolic trend. A polynomial fit was done and it can be seen in Figure 6.
The error on the spray amount was the standard deviation.
The minimum was found from fit data, it can be seen as the red point in the fit. Minimum coordinates value are also reported in the table in Figure 6.
Minimum coordinates value with the experimental data are compatible within the error range. (Figure 4)

	P = 1.6 bar		P = 4 bar	
	Fit		Experimental	
x	67 ± 25,8	75	59 ± 26,1	50
y	6,84 ± 2,48	4,19 ± 0,16	6,84 ± 2,48	7,17 ± 0,17

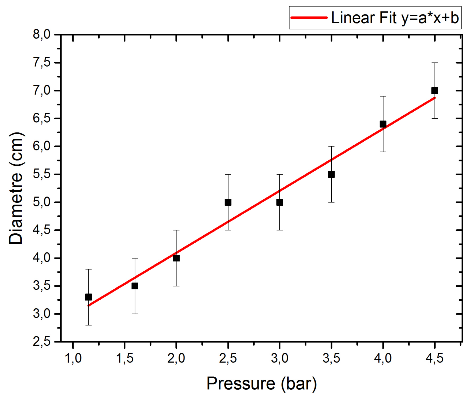
Figure 4: The tables show the minimum coordinates obtained from the fit and from the experimental data.

A linear fit was done on the diametre data.(Figure 7), that decrease by increasing the percentage of ethanol.

The spray amount per cm^2 was calculated from data, and results are in Figure 8.



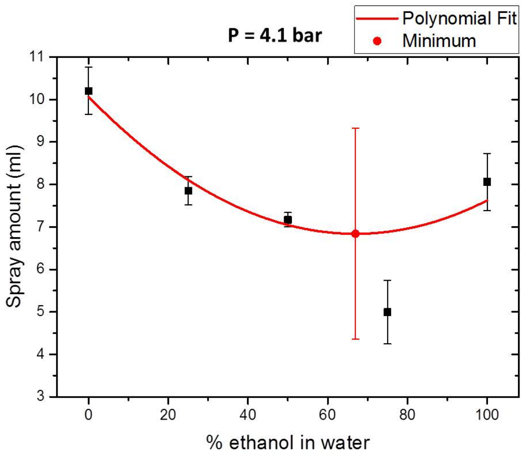
Intercept		Slope		Statistics
Value	Standard Error	Value	Standard Error	Adj. R-Square
1,12372	0,34546	1,97823	0,10905	0,98204



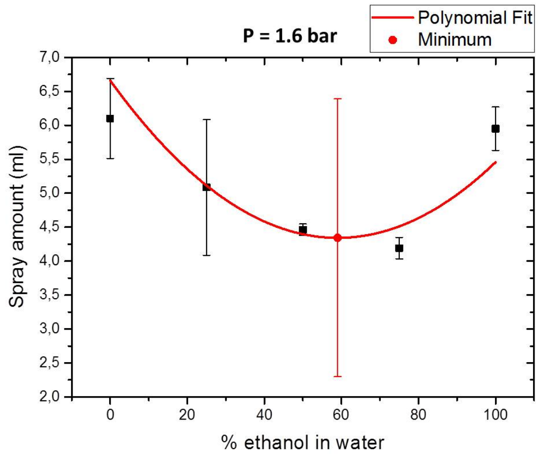
Intercept		Slope		Statistics
Value	Standard Error	Value	Standard Error	Adj. R-Square
1,87325	0,21787	1,11074	0,07281	0,97068

Figure 5: Linear fit of spray amount and diametre by varying the pressure. The error for each value is the standard deviation.
The spray amount measurement was performed using ethanol. The spraying was executed in one single cycle of 10 s and the pressure was varied from 1.5 to 4 bar. The heights 5 of different spray cycles were collected for each applied pressure.
The diametre measurement was performed using a tissue and measuring the diameter of the circle created by the sprayed ethanol solution.The spraying was executed in one single cycle of 10 s, the pressure was varied from 1.5 to 4 bar and the distanze nozzle to substrate was 15 cm.

The fit presents a positive slope of order 10^3 for P = 1.6 bar and of order 10^3 for P = 4 bar, as it can be seen in the table of the Figure 8.
The errors on spray amount per cm^2 data were obtained with the propagation of errors formula:
$\sigma_{f(x,y)} = \sqrt{(\frac{\partial f}{\partial x})^2 \cdot (\sigma_x)^2 + (\frac{\partial f}{\partial y})^2 \cdot (\sigma_x)^2}$

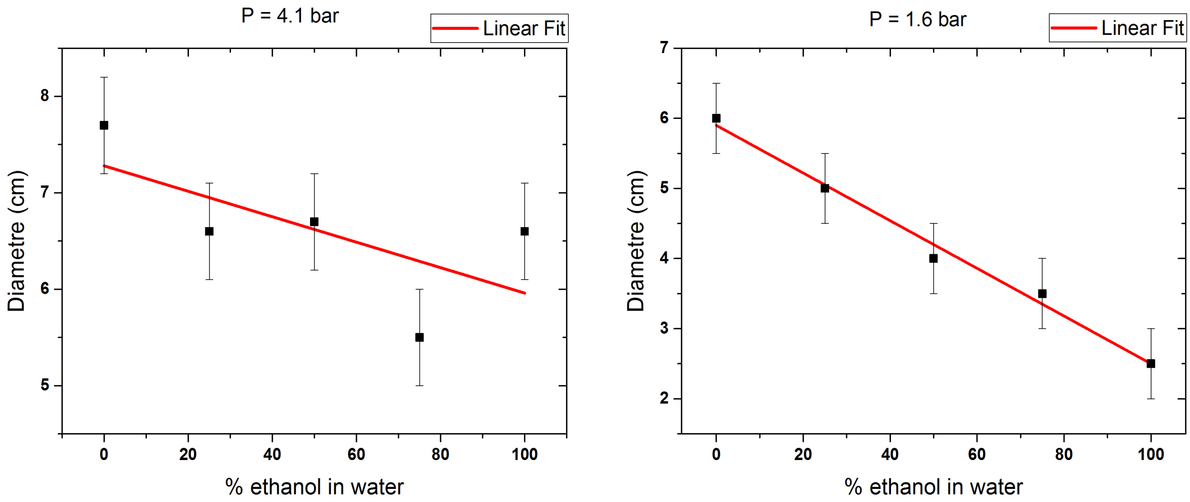


Equation	y = Intercept + B1*x^1 + B2*x^2
Intercept	10,0645 ± 0,9621
B1	-0,09631±0,0371
B2	7,19065E-4 ± 3,70091E-4
Adj. R-Square	6,05E-01
Minimum x	6,70E+01 ± 2,58+E01
Minumum y	6,84 ± 2,48



Equation	y = Intercept + B1*x^1 + B2*x^2
Intercept	6,6595 ± 1,0919
B1	-0,0785±0,0371
B2	7,19065E-4 ± 3,70091E-4
Adj. R-Square	6,05E-01
Minimum x	5,90+E01 ± 2,6+E01
Minumum y	4,34±2,04

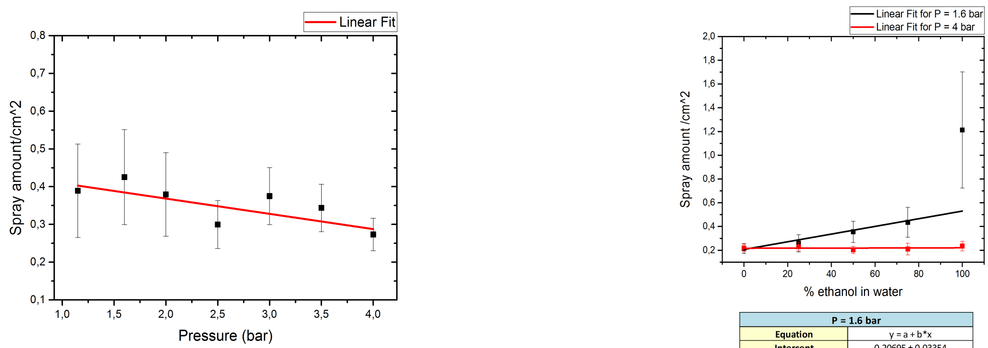
Figure 6: Polynomial fit of spray amount by varying the percentage of ethanol in distilled water. The error for each value is the standard deviation.
The spray amount and the diametre were measured at high pressure (P = 4.1 bar) and low pressure (P = 1.6 bar).
The spraying was executed in one single cycle of 10 s. To improve the statistics the heights of 5 different spray cycles were collected for each solvent.



Equation	$y = a \cdot x + b$
Intercept	7,28 ± 0,52
Slope	-0,0132 ± 0,0084
Adj. R-Square	0,2647

Equation	$y = a \cdot x + b$
Intercept	5,9 ± 0,1
Slope	-0,034 ± 0,002
Adj. R-Square	0,9863

Figure 7: Linear fit of mean diametre by varying the percentage of ethanol in distillated water. The error for each value is the standard deviation.
The diametre measurement was performed using a tissue and measuring the diameter of the circle created by the sprayed solution.
The spraying was executed in one single cycle of 10 s and the distanze nozzle to substrate was 15 cm.



Equation	y = a + b*x
Intercept	0,4492 ± 0,05629
Slope	-0,04043 ± 0,01711
Adj. R-Square	0,43299

P = 1.6 bar	
Equation	y = a + b*x
Intercept	0,20695 ± 0,03354
Slope	0,00323 ± 0,00114
Adj. R-Square	0,63751
P = 4 bar	
Equation	y = a + b*x
Intercept	0,21677 ± 0,01067
Slope	4,11098E-5 ± 1,96705E-4
Adj. R-Square	-0,3142

Figure 8: Spray amount per cm^2 by varying pressure and percentage of ethanol

5 Morphology analysis of sprayed $AgNO_3$ nanoparticles

5.1 Qualitative study

A qualitative study of samples is summarized in the following section.
Analyzing various samples obtained from a 10 to 100 mM/l $AgNO_3$ solution was useful to do a coarse study of $AgNO_3$ nanoparticles.
It can be seen that when decreasing the concentration the size of the obtained structures on the substrate will decrease.
For concentrations between 30 mM/l and 100 mM/l the structures are in the micrometer range(Figure 9).
Since this study aimed at nanoparticles formation, concentrations between 30 mM/l and 100 mM/l can be excluded.

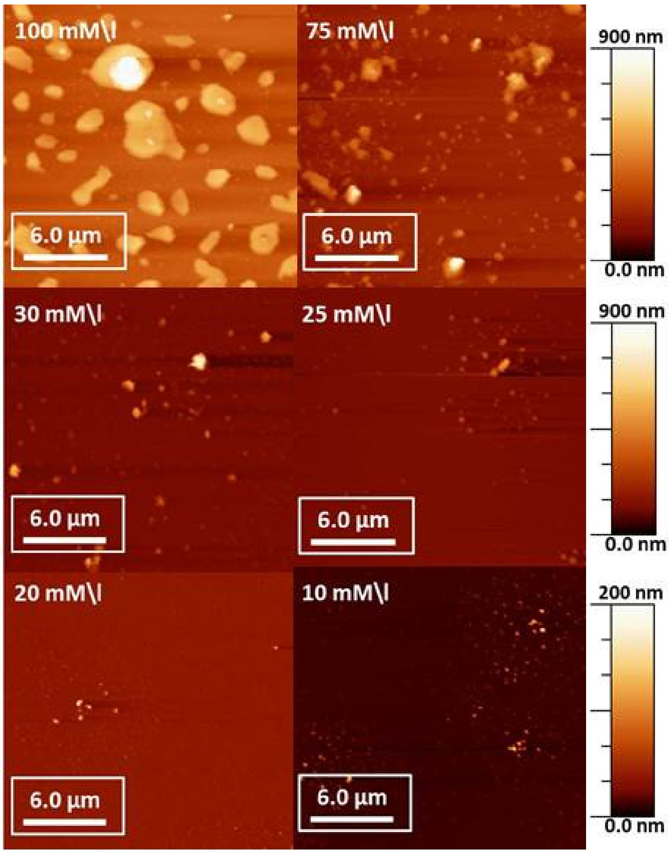


Figure 9: AFM image of nanoparticles obtained from a 10 to 100 mM/l $AgNO_3$ solution.The spraying was executed in one single cycle of 10 s, the pressure was 1.5 bar, the temperature was 120 °C and the distanze nozzle to substrate was 15 cm. It shows various concentration samples. When decreasing the concentration the size of the nanoparticles decrease.

The concentration range between 5 mM/l and 25 mM/l where this coarse study indicated

the nanoparticles formation was further analyzed and investigated in more detail.
It was found the same arrangement of nanoparticles: smaller nanoparticles are focused around organized group of larger nanoparticles (Figure 10).
Between this groups a quite homogeneous distribution can be found. It can be point out in Figure 11.
Analyzing smaller images it can be noticed that when decreasing the concentration the number of nanoparticles/area decreases. (Figure 12.**I.**)
An attempt was made to find a trend with a linear fit, as it can be seen in (Figure 12.**II.**)

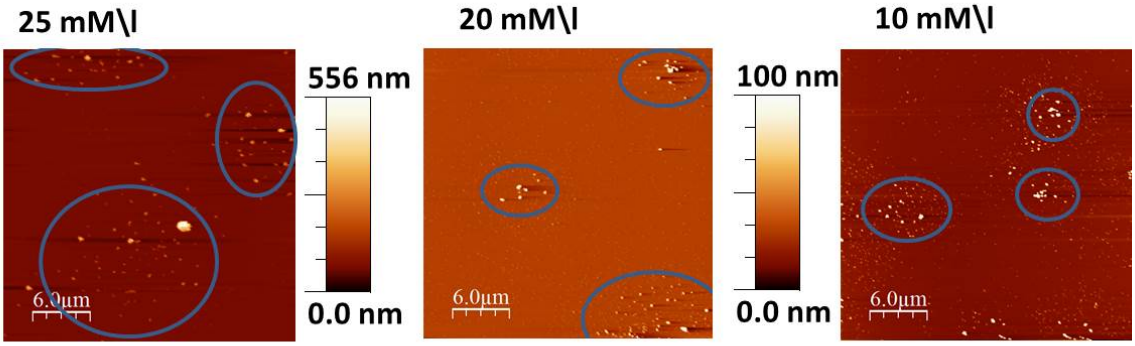


Figure 10: AFM image of nanoparticles obtained from 25,20,10 mM/l $AgNO_3$ solution. The spraying was executed in one single cycle of 10 s, the pressure was 1.5 bar, the temperature was 120 °C and the distanze nozzle to substrate was 15 cm. It shows various concentration samples. It shows the same arrangement for lower concentration samples.

5.2 Quantitative study

A quantitative study was made collecting diametre and height data of 20 nanoparticles for concentration of 5,10,20,25 mM/l. A fit with a Gaussian function on the peaks was done.(Figure 12.**III**) and (Figure 12.**IV**)
For each peak were considered the full width at half maximum and the height and it was made the average on the values obtained.
Plot in Figure 13 shows how height and diameter vary according to the concentration.

5.3 Conclusions

In the quantitative study it can be seen that the number of nanoparticle/area has a linear trend for 5 , 10, 20 mM/l sample
Data concerning diametre and height of 25 mM/l sample were excluded, beacause they present a lower density. Further analysis were made to estimate height and diametre and from the figure 13 a bigger height and diametre for 25 mM/l were found, but their values are included in the error range.

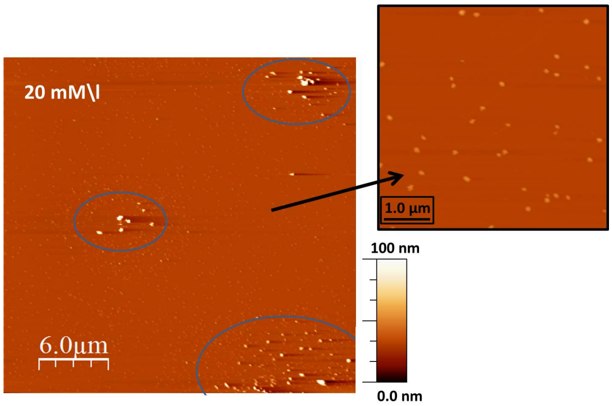


Figure 11: AFM image of nanoparticles obtained from 20 mM/l $AgNO_3$ solution. It shows the homogeneous nanoparticles distribution between group of larger nanoparticle.

6 Summary and outlook

This work allowed a first characterization of the nanoparticle formation from silver nitrate.
From the analysis of the spray system it was possible to understand that the spray amount and the diametre depend linearly on the pressure, the spray amount depends on the percentage of ethanol in water following a parabolic trend and the diametre depends linearly on the percentage of ethanol in water.
This colud be important to undestand how the nanoparticles growth can be varied, and for the preparation of new samples.
From the morphology analysis it was pointed out that nanometric structure can be found in the concentration range between 5 mM/l and 25 mM/l. In this range nanoparticle seems to have the same arrangment for the analyzed concentrations.
The number of nanoparticle/area increases with the concentration, but the sample obtained from 25 mM/l $AgNO_3$ solution resulted with a lower density and bigger size of nanoparticles.
About the AFM technique, it presents a big limitation: only a small area can be probed in one measurement and the acquisition of many images is necessary to obtain reliable statistic.
Future studies could be performed with the GISAXS technique. Due to the gracing incidence geometry with the small incident angle, this technique allows to investigate a large area and thus a statistical description of the sample over macroscopic lenght scale is obtained.

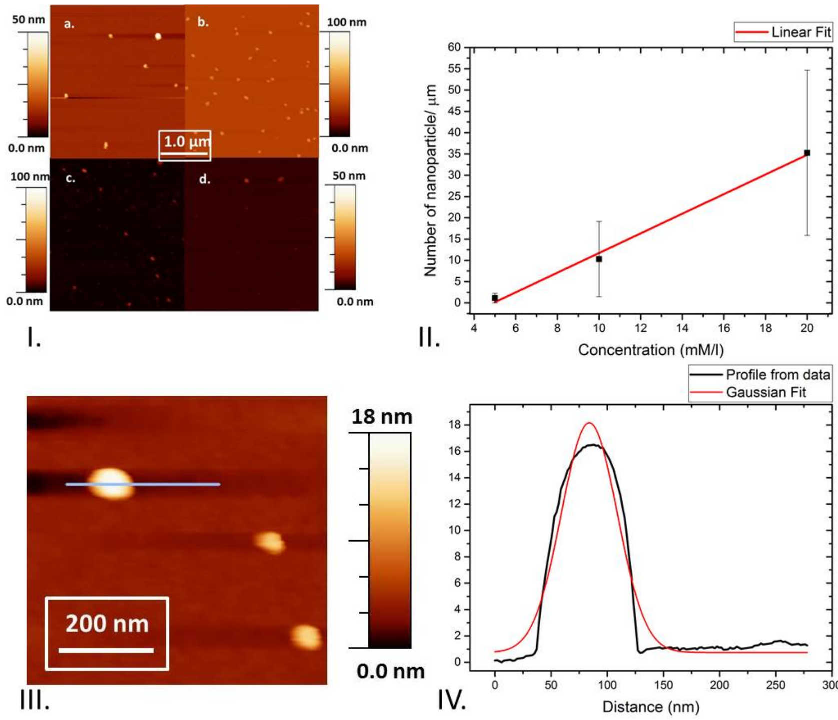


Figure 12: **I.** AFM image of nanoparticles obtained from 25 mM/l (**a.**), 20 mM/l (**b.**), 10 mM/l (**c.**), 5 mM/l (**d.**) $AgNO_3$ solution. **II.**Linear fit of the number of nanoparticle/area varying the concentration. **III.** AFM image of nanoparticles obtained from 20 mM/l $AgNO_3$ solution. **IV** A nanoparticle profile obtain from data of 20 mM/l sample and its gaussian fit.

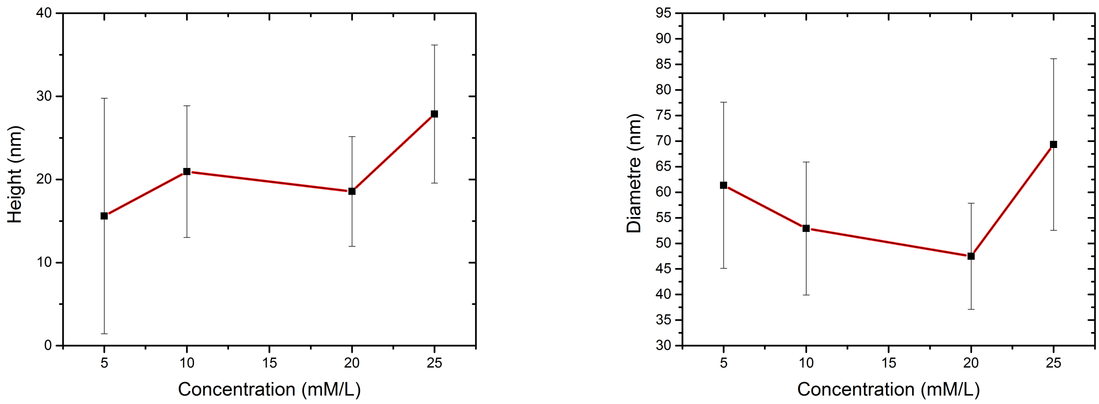


Figure 13: Mean height and mean diametre of nanoparticles trend by increasing concentration of $AgNO_3$ solution.

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