Journal of Kerbala University , Vol. 11 No.4 Scientific . 2013

study the optimum conditions of synthesis AgNP by chemical reduction method

دراسة الظروف القياسية لتحضير جسيمات الفضة النانوية بطريقة الاختزال الكيميائي

Bahaa T.Chiad Natheera.A.Ali Zainab.S. Sadik Sarmed. S.AL-Awadi
Department of Physics, College of Science, University of Baghdad, Jadiria, Baghdad, Iraq.

Abstract :-

In this paper, silver nanoparticles had been prepared by chemical reduction method. Many tests had been done to it such as UV-Visible spectrophotometer, XRD, AFM&SEM test. finally an attempt had been done to get the optimum condition to control the grain size of silver Nanoparticles by variation the heating period and other parameters which has an effect in silver Nanoparticles synthesis process. in this method we can get a silver nanoparticles in the size range from 52 to 97 nm.

الخلاصة :-

تضمنت الدراسة الحالية تحضير جسيمات الفضة النانوية بطريقة الاختزال الكيميائي. عدة قياسات اجريت للنماذج المحضرة كقياس مطيافية الاشعة تحت الحمراء وفوق البنفسجية لقياس الامتصاصية بالاضافة الى حيود الاشعة السينية ومقياس القوى الذرية فضلا عن استخدام المجهر الالكتروني الماسح.فضلا عن كل هذا يهدف هذا البحث الى اجراء دراسة تفصيلية لدراسة امكانية السيطرة على حجم جسيمات الفضة النانوية من خلال دراسة المتغيرات التي من الممكن ان تؤثر على عملية التحضير كتغيير زمن الاختزال وباقي المتغيرات الاخرى .في هذه الطريقة من الممكن ان نحضر جسيمات فضة نانوية تتراوح احجامها بين 52 الى 97 نانومتر .

INTRODUCTION :-

One of the first and most natural questions to ask when starting to deal with nanoparticles is: "why are nanoparticles so interesting"?. Why even bother to work with these extremely small structures when handling and synthesis is much more complicated than that of their macroscopic counterparts ?.The answer lies in the nature of and unique properties possessed by nanostructures.[1] as a consequence to that There is a huge interest in metal nanoparticles because of their unexpected physical and chemical properties shown at nanoscale. Metal nanoparticles could be key elements for applications in optics, spectrscopy and electronics mainly because of the quantized motion of the collectively excited conduction electrons, the size dependent 'surface plasmons', which results in extraordinary large electromagnetic field enhancements, upon interaction with an incoming electromagnetic field [2]. Silver nanoparticles have received considerable attention due to their attractive physical and chemical properties. Metallic silver colloids were first prepared more than a century ago. Ag nanoparticles can be synthesized using various methods: chemical, electrochemical [3], γ-radiation [4] photochemical [5], laser ablation [6] etc. The most popular preparation of Ag colloids is chemical reduction of silver salts by sodium borohydride or sodium citrate [7]. This preparation is simple, but the great care must be exercised to make stable and reproducible colloid. The purity of water and reagents, cleanliness of the glassware are critical parameters. Solution temperature, concentrations of the metal salt and reducing agent, reaction time influences particle size. Controlling size and shape of metal nanoparticles remains a challenge [8]. The size-induced properties of nanoparticles enable the development of new applications or the addition of flexibility to existing systems in many areas, such as catalysis, optics, microelectronics and so on.

Experimental part :-

Chemical Materials

The silver nitrate (99% $AgNO_3$), Sodium citrate tribasic dehydrate (99% $C_6H_5Na_3O_7.2H_2O$) was purchased from Sigma-Aldrich. Distilled water was used.

Synthesis of Ag nanoparticles:-

We try to prepares $1x10^{-3}$M of Ag Colloids (Sodium Citrate Reduction Method)

1.we prepared a 50 ml as a starting solution of ~ 5.0 x 10^{-3}M $AgNO_3$ in water. (0.0425 g in 50mL deionizedH_2O). then we Take 25mL of that solution and add it to another 100mL of H_2O (now ~1.0 x 10^{-3}M).in another hand we Make a solution of 1% sodium citrate (0.5 g in 50mLof H_2O) then we Heat the 125mL solution of $AgNO_3$until it begins to boil at 97 C. at a moment of boiling we start to Add 5mL of 1% sodium citrate solution drop by drop , as soon as boiling commences. We Continue heating for 5 minutes until color change is evident (pale yellow) we repeat the experiment for 6,7,8,9&10 minutes from boiling point then we Remove the solution from the heating element and continue to stir until it has cooled to room temperature. we take the absorption spectra for each solution after 10 minutes from removing it from heating .

Analysis technique :-

The optical properties (absorbance) of colloidal solution were evaluated with UV/VIS/NIR spectrophotometer (Metertech UV-Vis SP8001), light source – combined deuterium-halogen, wavelength range: 200 nm –1100 nm.AFM study carried out by (AA3000, Angstrom Advanced Inc. USA). The morphology of siver nanoparticles was observed by

using JEOL JSM-5200 scanning electron microscope oper ating at 15 kV at a magnification of 10,000×.The formation of silver nanoparticles was identified by the XRD (Rigaku)

Results and discussion:-

Figure (1) below represent the total absorption spectra of Ag colloidal which is prepared by chemical reduction method for different reduction periods of heating after boiling point for $AgNO_3$ solution, from the first sight to this figure on can observe that the absorption intensity increase with increasing the heating period while, the maximum peak absorption for surface plasmon of silver nanoparticles which has a 5 minute as a reduction period was occurred at 425 nm and for 6&7 minutes was occurred at 426nm while for 8,9,10 minutes was occurred at 428,429 and 439 nm respectively this manner is clearly illustrated in figure 1 and this means that the general manner of peak absorption for silver nanoparticles as a function to reduction periods is "red shift", this red shift may be attributed to increasing the concentration of AgNP by aggregation formation with increasing the reduction period.

Figure 2 represent the absorbance intensity as a function to reduction period on an see that the absorbance intensity was increased with increasing the reduction period where as when reduction time increase the nanoparticles aggregation had been formed and that is lead to increase the AgNP concentration as a consequence to that the absorbance intensity increased with increasing AgNP concentration and this manner agree with beer Lambert laws. While the variation of FWHM with reduction period had been illustrated in figure 3 it is quite clearly in figure that FWHM was decreased with increasing reduction period from 5 to 9 minutes except at the case of 10 minute but it still narrow width if it compared with the FWHM at the case of 5 minutes.figure 4 show the X-ray diffraction for silver nanoparticles which is prepared by chemical reduction method,while Figure 5 show the atomic force microscope results for AgNP which had been prepared in different reduction periods, one can observed that the particle size was variated from 73 to 85 nm and it is so difficult to controlling the grain size so it is a global problem but the particle size still in the nanoparticle range, in the point of view of our research group we advice to prepared AgNP with tiny reduction

periods like 5 minutes of smaller than.while figure 5 show the SEM resultes for 5&10 minutes as a redction time . All these results as well as silver particle size had been illustrated in table 1

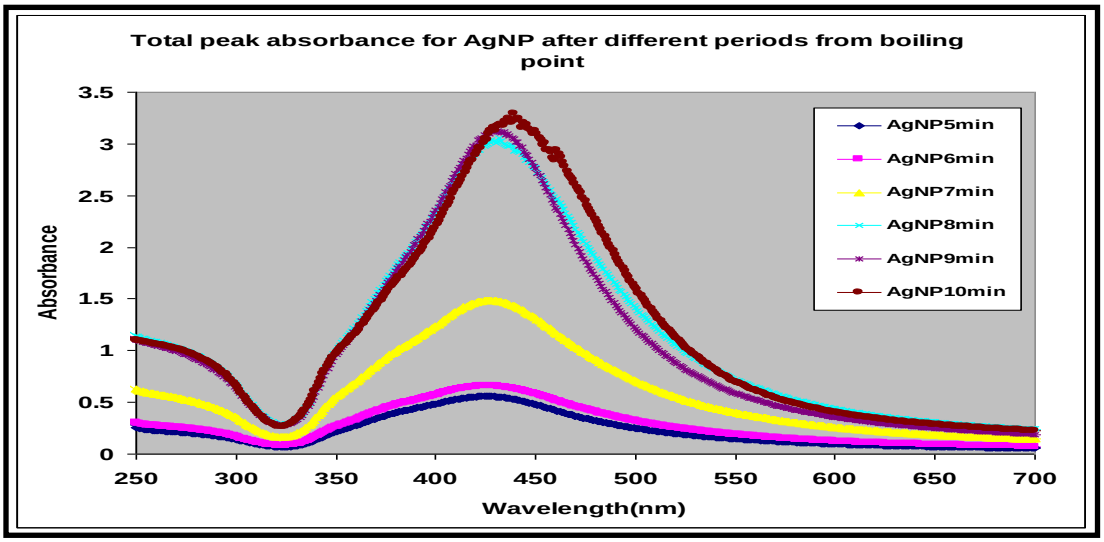


Figure (1) showthe total absorption spectra of Ag colloidal which is prepared by chemical reduction method for different reduction periods

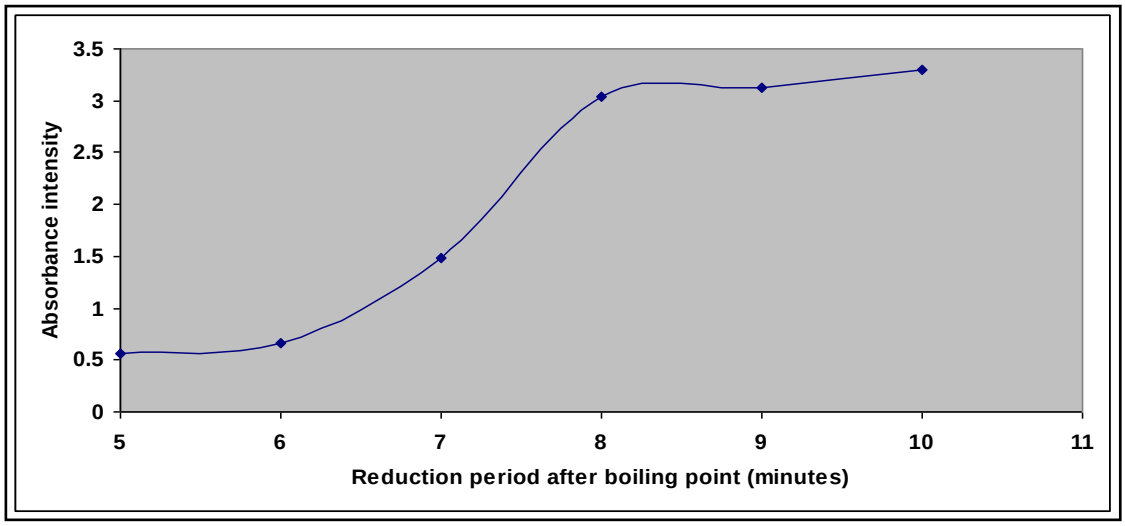


Figure (2) show the absorbance intensity as a function to reduction period

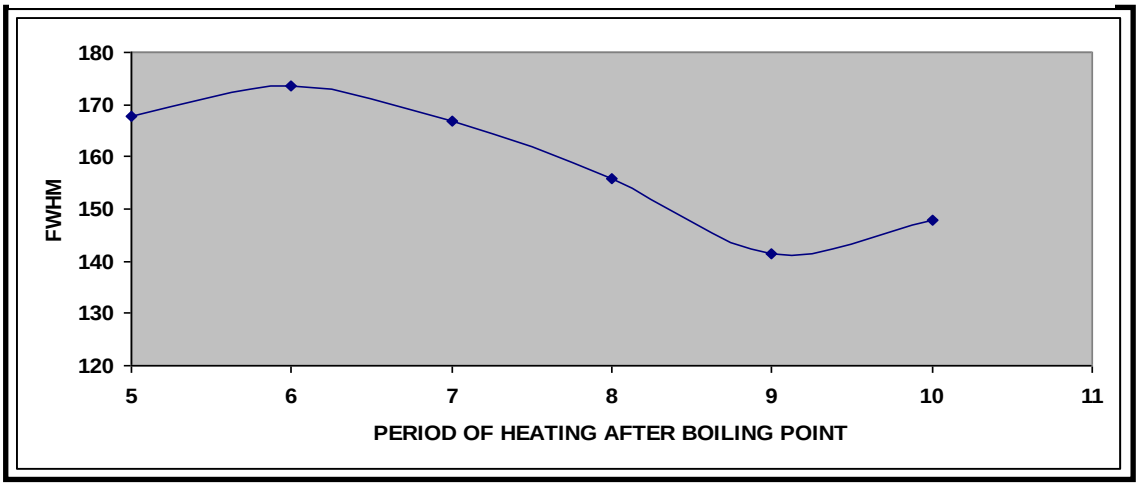


Figure (3) show the the variation of FWHM with reduction period

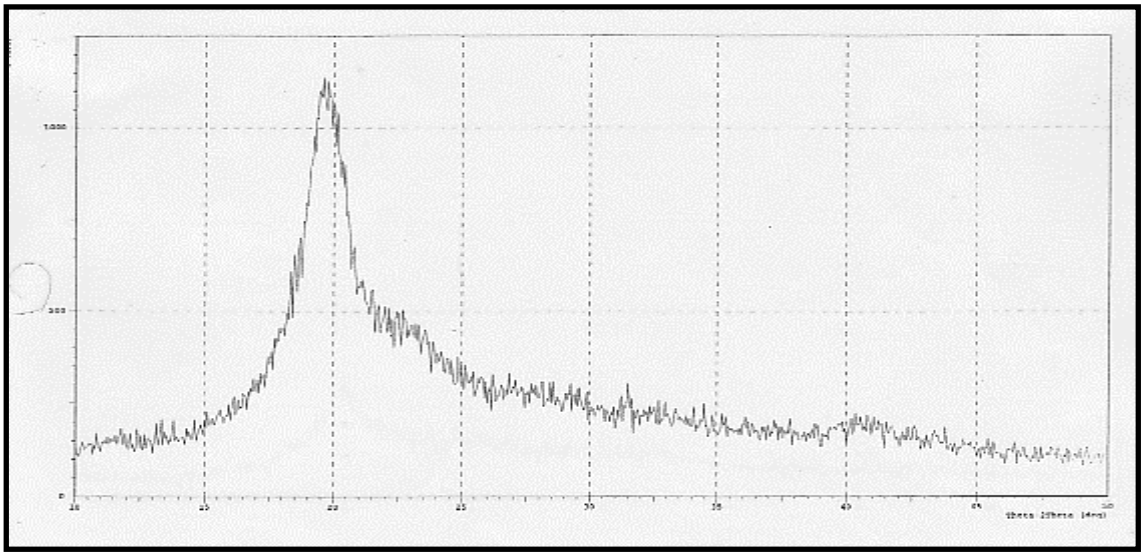
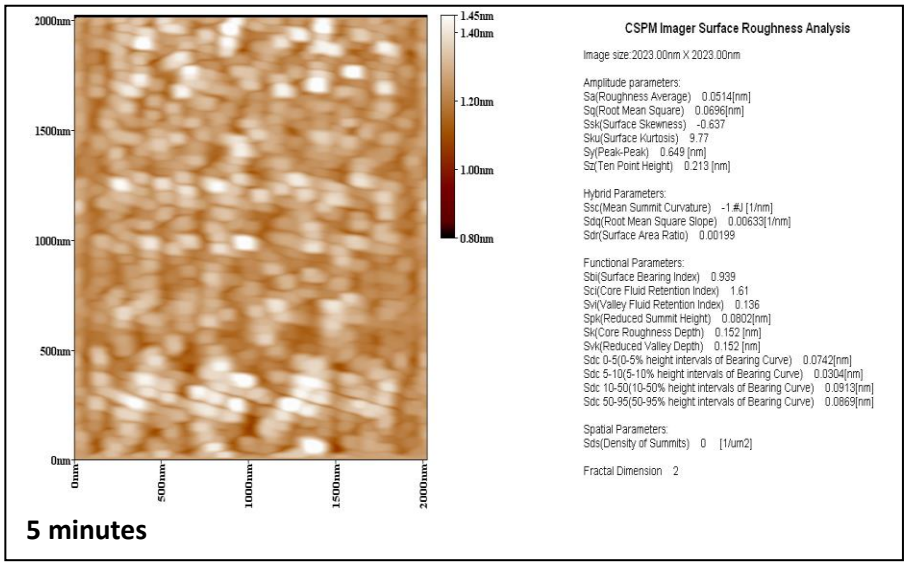
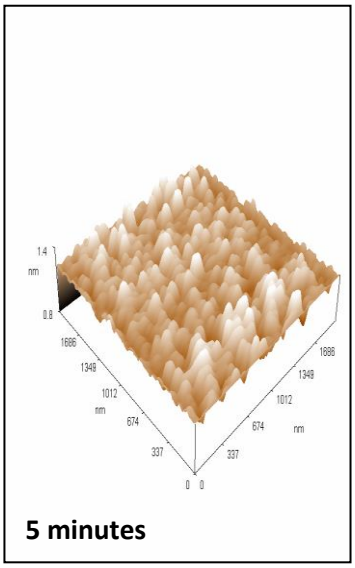
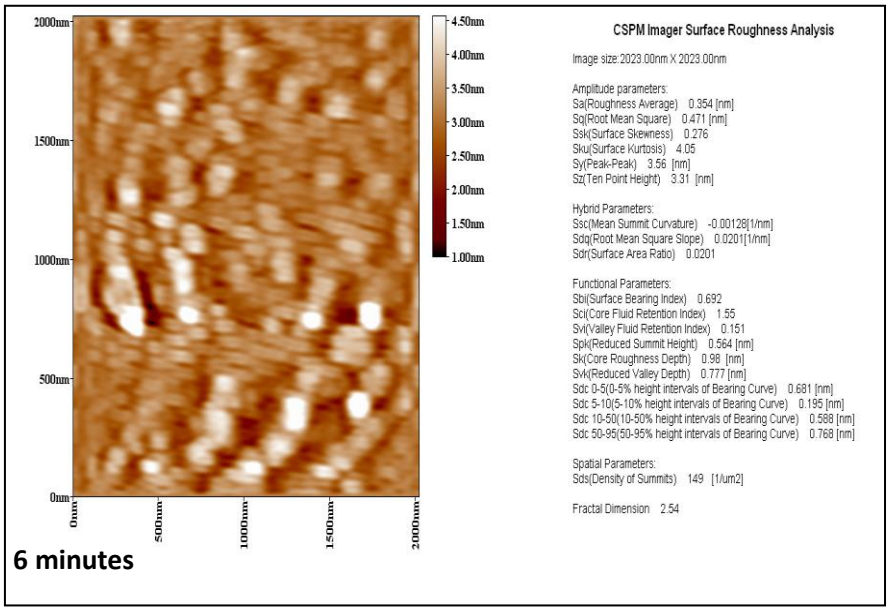
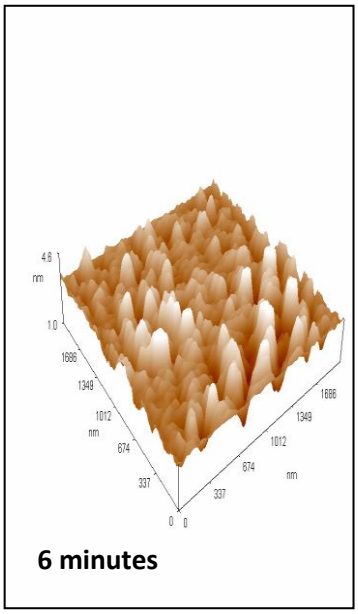


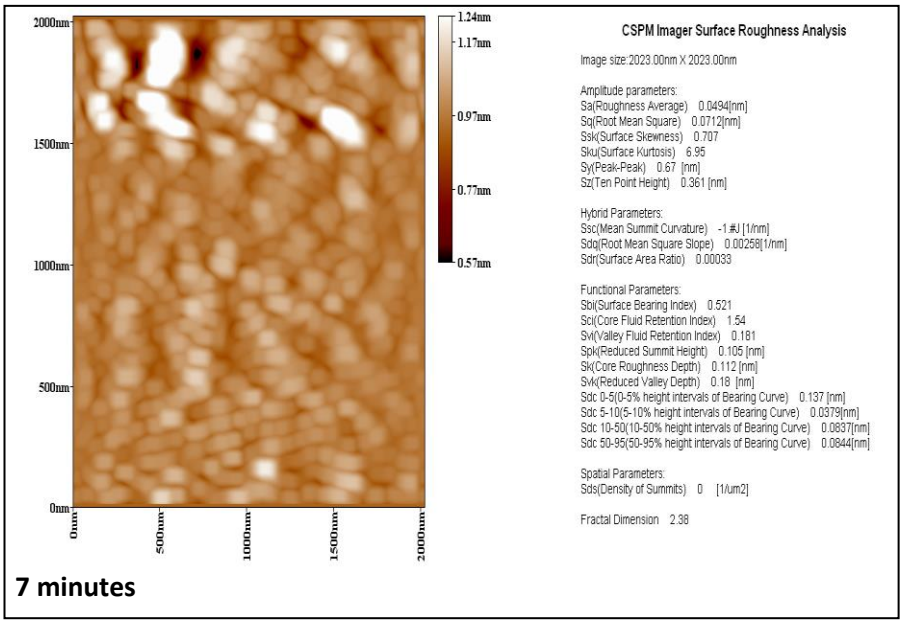
Figure 4 show the X-ray diffraction patterns for AgNP which is prepared by chemical reduction method

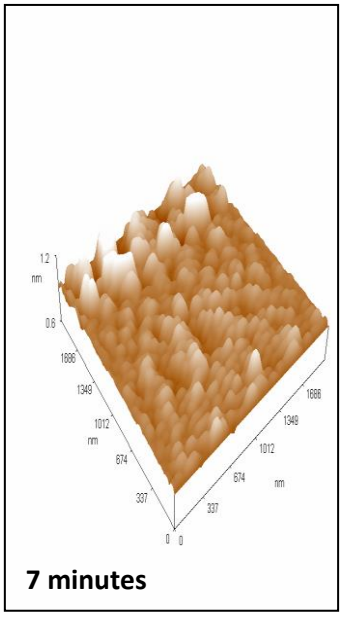


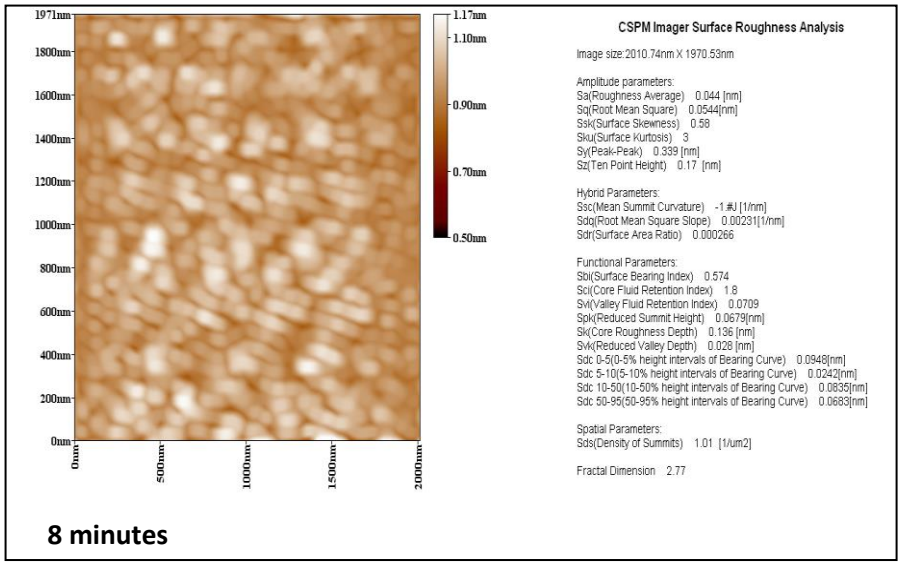


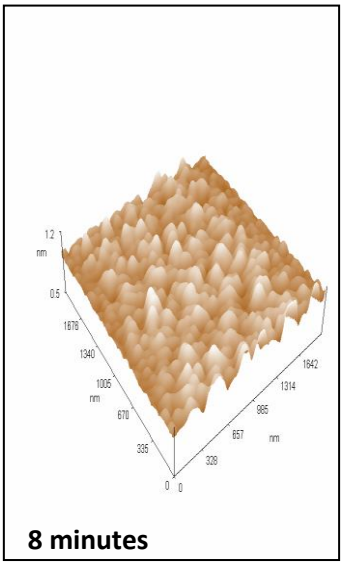


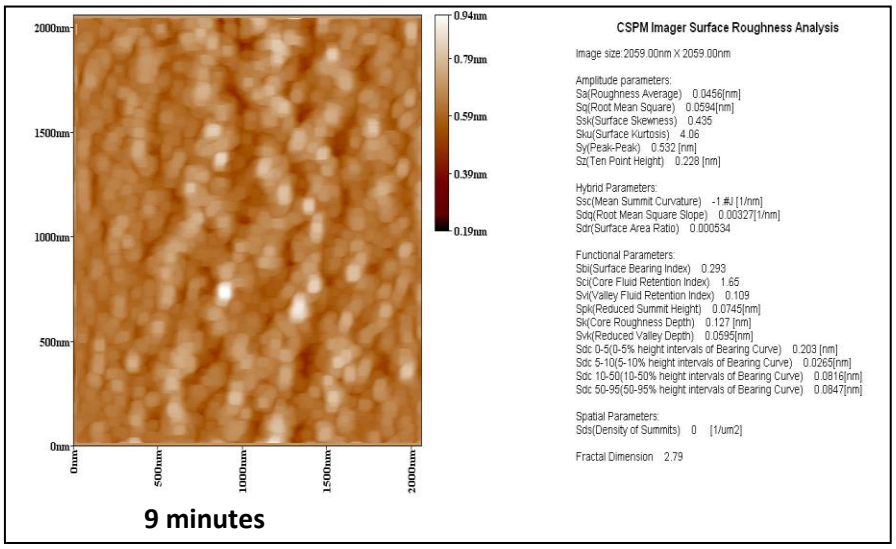


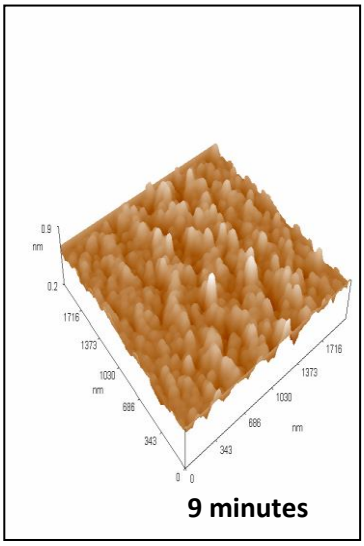

CSPM Imager Surface Roughness Analysis
Image size:2023.00nm X 2023.00nm
Amplitude parameters:
Sa(Roughness Average) 0.0494[nm]
Sq(Root Mean Square) 0.0712[nm]
Ssk(Surface Skewness) 0.707
Sku(Surface Kurtosis) 6.95
Sy(Peak-Peak) 0.67 [nm]
Sz(Ten Point Height) 0.361 [nm]
Hybrid Parameters:
Ssc(Mean Summit Curvature) -1.#J [1/nm]
Sdq(Root Mean Square Slope) 0.00258[1/nm]
Sdr(Surface Area Ratio) 0.00033
Functional Parameters:
Sbi(Surface Bearing Index) 0.521
Sci(Core Fluid Retention Index) 1.54
Svi(Valley Fluid Retention Index) 0.181
Spk(Reduced Summit Height) 0.105 [nm]
Sk(Core Roughness Depth) 0.112 [nm]
Svk(Reduced Valley Depth) 0.18 [nm]
Sdc 0-5(0-5% height intervals of Bearing Curve) 0.137 [nm]
Sdc 5-10(5-10% height intervals of Bearing Curve) 0.0379[nm]
Sdc 10-50(10-50% height intervals of Bearing Curve) 0.0837[nm]
Sdc 50-95(50-95% height intervals of Bearing Curve) 0.0844[nm]
Spatial Parameters:
Sds(Density of Summits) 0 [1/um2]
Fractal Dimension 2.38
7 minutes


7 minutes


CSPM Imager Surface Roughness Analysis
Image size:2010.74nm X 1970.53nm
Amplitude parameters:
Sa(Roughness Average) 0.044 [nm]
Sq(Root Mean Square) 0.0544[nm]
Ssk(Surface Skewness) 0.58
Sku(Surface Kurtosis) 3
Sy(Peak-Peak) 0.339 [nm]
Sz(Ten Point Height) 0.17 [nm]
Hybrid Parameters:
Ssc(Mean Summit Curvature) -1.#J [1/nm]
Sdq(Root Mean Square Slope) 0.00231[1/nm]
Sdr(Surface Area Ratio) 0.000266
Functional Parameters:
Sbi(Surface Bearing Index) 0.574
Sci(Core Fluid Retention Index) 1.8
Svi(Valley Fluid Retention Index) 0.0709
Spk(Reduced Summit Height) 0.0679[nm]
Sk(Core Roughness Depth) 0.136 [nm]
Svk(Reduced Valley Depth) 0.028 [nm]
Sdc 0-5(0-5% height intervals of Bearing Curve) 0.0948[nm]
Sdc 5-10(5-10% height intervals of Bearing Curve) 0.0242[nm]
Sdc 10-50(10-50% height intervals of Bearing Curve) 0.0835[nm]
Sdc 50-95(50-95% height intervals of Bearing Curve) 0.0683[nm]
Spatial Parameters:
Sds(Density of Summits) 1.01 [1/um2]
Fractal Dimension 2.77
8 minutes


8 minutes


CSPM Imager Surface Roughness Analysis
Image size:2059.00nm X 2059.00nm
Amplitude parameters:
Sa(Roughness Average) 0.0456[nm]
Sq(Root Mean Square) 0.0594[nm]
Ssk(Surface Skewness) 0.435
Sku(Surface Kurtosis) 4.06
Sy(Peak-Peak) 0.532 [nm]
Sz(Ten Point Height) 0.228 [nm]
Hybrid Parameters:
Ssc(Mean Summit Curvature) -1.#J [1/nm]
Sdq(Root Mean Square Slope) 0.00327[1/nm]
Sdr(Surface Area Ratio) 0.000534
Functional Parameters:
Sbi(Surface Bearing Index) 0.293
Sci(Core Fluid Retention Index) 1.65
Svi(Valley Fluid Retention Index) 0.109
Spk(Reduced Summit Height) 0.0745[nm]
Sk(Core Roughness Depth) 0.127 [nm]
Svk(Reduced Valley Depth) 0.0595[nm]
Sdc 0-5(0-5% height intervals of Bearing Curve) 0.203 [nm]
Sdc 5-10(5-10% height intervals of Bearing Curve) 0.0265[nm]
Sdc 10-50(10-50% height intervals of Bearing Curve) 0.0816[nm]
Sdc 50-95(50-95% height intervals of Bearing Curve) 0.0847[nm]
Spatial Parameters:
Sds(Density of Summits) 0 [1/um2]
Fractal Dimension 2.79
9 minutes


9 minutes

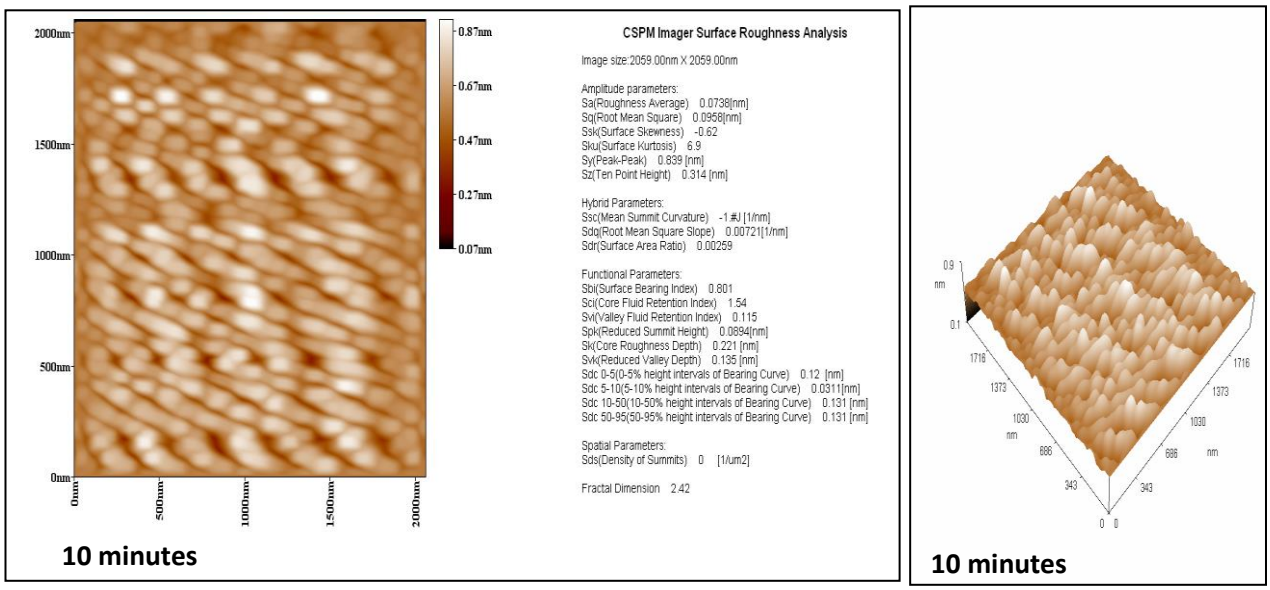


Figure 5 illustrated the Atomic Force Microscope results for silver nanoparticles which is prepared with different reduction periods

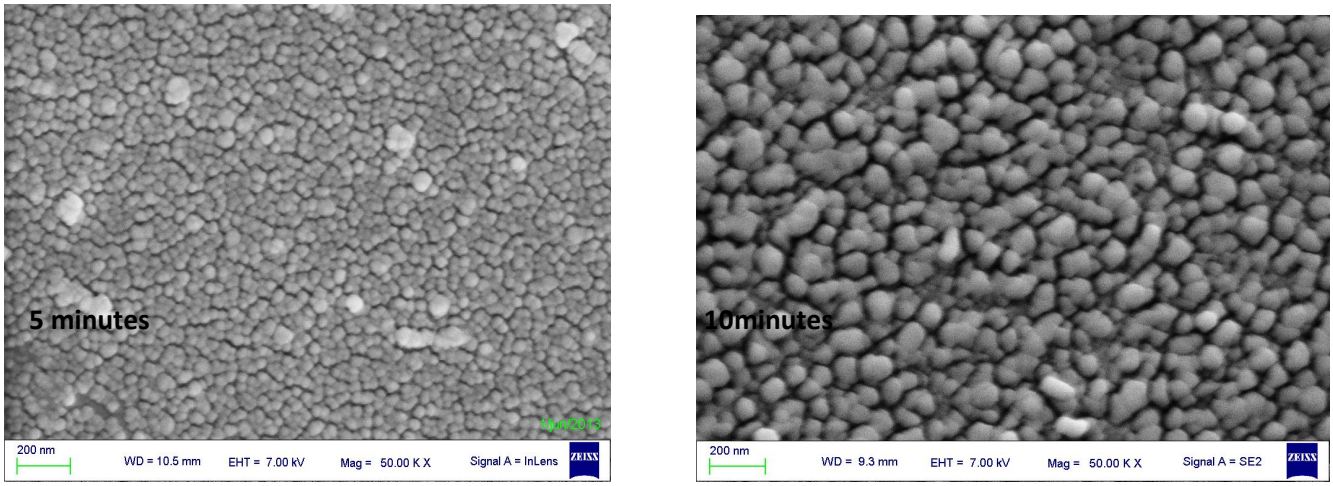


Figure 6 show the Scanning Electron Microscope results for silver nanoparticles for 5&10 minutes reduction

Table 1 show the different calculations & results for AGNP which is prepared by chemical reduction method in different reduction periods

Reduction time after boiling point(minute)	Maximum peak absorbance(nm)	FWHM (nm)	Absorbance intensity (a.u)	Particles size (nm)
5	425	167.67	0.5581	73.32
6	426	173.65	0.6582	52.70
7	426	166.7	1.4839	97.87
8	428	155.76	3.0353	84.29
9	429	141.48	3.1248	79.99
10	439	147.96	3.2926	85.98

Conclusions :-

The minimum particle size for silver nanoparticles which is prepared by chemical reduction method can be obtain by choosing a short reduction period while increasing the reduction period will be lead to aggregation formation &the controlling of particle size by this method is very complicated and difficult.

References :-

[1]Maribel G. Guzman, Jean Dille and Stephan Godet **"Synthesis of silver nanoparticles by chemical reduction method and their antibacterial activity"** International Journal of Chemical and Biological Engineering **2:3 2009**

[2]Kreibig, U., Vollmer, M. **Optical Properties of Metal Clusters.** Springer, Berlin**,: pp. 203 – 275. 1995**

[3]Vorobyova, S. A., Lesnikovich, A. I., Sobal, N. S. **Preparation of Silver Nanoparticles by Interphase Reduction Colloids and Surfaces A:** Physicochemical and Engineering Aspects 152 **1999: pp. 375 – 379.**

[4]Choi, S. H., Zhang, Y. P., Gopalan, A., Lee, K. P., Kang,H. D. **Preparation of Catalytically Efficient Precious Metallic Colloids by □-irradiation and Characterization Colloids and Surfaces A:** Physicochemical and Engineering Aspects 256 **2005: pp. 165 – 170.**

[5]Li, Z., Li, Y., Qian, X. F., Yin, J., Zhu, Z. K. A **Simple Method for Selective Immobilization of Silver Nanoparticles** Applied Surface Science 250 **2005: pp. 109 – 116**.

[6]Tsuji, T., Watanabe, N., Tsuji, M. **Laser Induced Morphology Change of Silver Colloids**: Formation of Nano-size Wires Applied Surface Science 211 **2003: pp. 189 – 193.**

[7]RATYAKSHI* and R.P. CHAUHAN **Colloidal Synthesis of Silver Nano Particles** Asian Journal of Chemistry **Vol. 21, No. 10 (2009), p114**

[8]Bell, W. C., Myrick, M. L. **Preparation and Characterization of Nanoscale Silver Colloids by Two Novel Synthetic Routes** Journal of Colloid and Interface Science 242 **2001: pp. 300 – 305.**