

## Synthesis of Silver Nanoparticles by Electrochemical Method

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### Abstract

In this present study, we present a method for the preparation of electrochemical silver nanoparticles .we employed two electrodes of pure silver with length 8-12 cm, thickness of 0.4 mm and width 8-10 mm inside a container full of DDDW with distance 10 mm between them and with potential difference about 27 volt.

For the purpose of analyzing of optical, structural and morphological properties of the surface that describe the nature, the charging and the voltages of these materials by using the UV-VIS, X-ray, Z-potential, SEM, AFM, and TEM were employed. Size and properties were controlled in high concentrations with good stability for long period without aggregation. Colloidal silver-NPs with grain size of 30-50 nm had been produced at optimum conditions.

**Key words:** silver nanoparticles, electrochemical, colloidal.

### تصنيع جسيمات الفضة النانوية بطريقة الكهروكيميائية

الخلاصة:

في هذه الدراسة، وظفت الطريقة الكهروكيميائية لتحضير جسيمات الفضة النانوية. إذ استخدم قطبين من الفضة النقية بطول 8-12 ملم وسمك 0.4 ملم وعرض يتراوح بين 8-10 ملم وضعت داخل حاوية تحتوي على ماء مقطر لا يوتي المسافة بين القطبين كانت 10 ملم والهد المسلط بينهم مساوي الى 27 فولت. لغرض تحليل الخصائص البصرية والتركيبية والطوبوغرافية لسطح ولمعرفة نوع شحنة وجهد السطح استخدم جهاز مطيافية الأشعة فوق البنفسجية والمرئية وجيود الأشعة السينية وجهد زيتا والمجهر الإلكتروني الماسح ومجهر القوى الذرية ومجهر الإلكتروني النافذ. تم السيطرة على حجم ووصفات واستقرارية العالقترة طويلة بدون تكتل عند التراكيز العالية. وكانت حجوم الفضة النانوية كعالق يتراوح بين 30-50 نانوميتر عند احسن الظروف. **الكلمات المفتاحية:** جسيمات الفضة النانوية، الكهروكيميائية، عالق.

### INTRODUCTION

The electrochemical techniques are quite interesting because they allow obtaining particles with a high purity using fast and simple procedures and controlling the particle size easily by adjusting the current density [1,2]. Through these techniques particles are obtained with determined size and shape [3,4] of several compositions [5-9]. In addition, this method is eco-friendly because it avoids the use of reducer agents that usually are toxic. Different stabilizers can be used in electrochemical techniques, which include organic monomers as electrostatic stabilizers [5] and polymeric compounds as steric stabilizers [10]. Ionic organic compounds can act as stabilizers and support electrolytes simultaneously avoiding the use of additional chemicals [5]. Thus, they are useful to several applications as

Surface-enhanced Raman Scattering techniques and others. The vast majority of products labeled and sold as *colloidal silver* fall into this category due to the low degree of manufacturing complexity and resulting low cost of production. Silver content in these products consists of both silver ions and silver particles. Typically, 90% of the silver content is in the form of *ionic silver* and the remaining 10% of the silver content is in the form of silver particles. The silver ions are produced by electrolysis and may be described as “dissolved silver”. Products produced by electrolysis are frequently described as “electro colloids”. Because the majority of the silver content in these products is *dissolved* silver rather than metallic silver particles, it would be more technically accurate to describe these products as *silver solutions*.

In the present work, electrochemical synthesis of silver nanoparticles is presented.

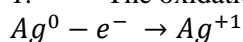
### Experimental work

The characterizations of the electrochemical method for producing nanoparticles can be described by high purity particles and the possibility to control the size of the nanoparticles through controlling the current density. This method is easy and effective for producing nanoparticles without using chemicals and maintains the stability.

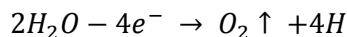
This method includes using two electrodes, Anode and Cathode plates made of silver with high purity reaches to 99.99% with dimensions (4 mm x 10 mm x 80 mm). The two electrodes are placed facing each other in a vertical way with a distance 10 mm between each other, the set up is placed in to electrical cell that contains 500 ml double distilled and deionised water (DDDW) obtained from (Center of Nanotechnology and Advanced Materials, University of Technology, Iraq). The silver particles precipitate on the cathode during the electrolysis. The electrolysis has been employed with the temperatures (30-70) K with continuous various voltages (25-28) V, the current passed in the circuit has been monitored with a voltmeter. Additionally, the electrical circuit has been controlled to change Polarity between the electrodes according the optimal period of 4 minutes. The production of nanoparticles in a manner of electrochemical reduction lies in changing the polarity of the direct current between the poles in addition to the steering during the electrolysis process in order to prevent the precipitation.

Figure (1) shows the process of formation of colloidal silver nanoparticles in the electrochemical method as follows:

1. The oxidation of silver at the anode as shown below:



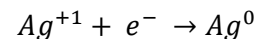
2. The release of oxygen gas due to the electrolysis of water:



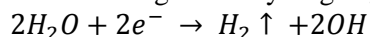
At the same time the deposition layer of  $Ag_2O$  on the surface of the anode.

3. Immigration of the silver ions to the cathode.

4. Reduction of the ions and formation of the silver atoms on the cathode:



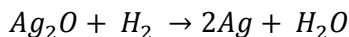
The releasing of the hydrogen gas during the process.



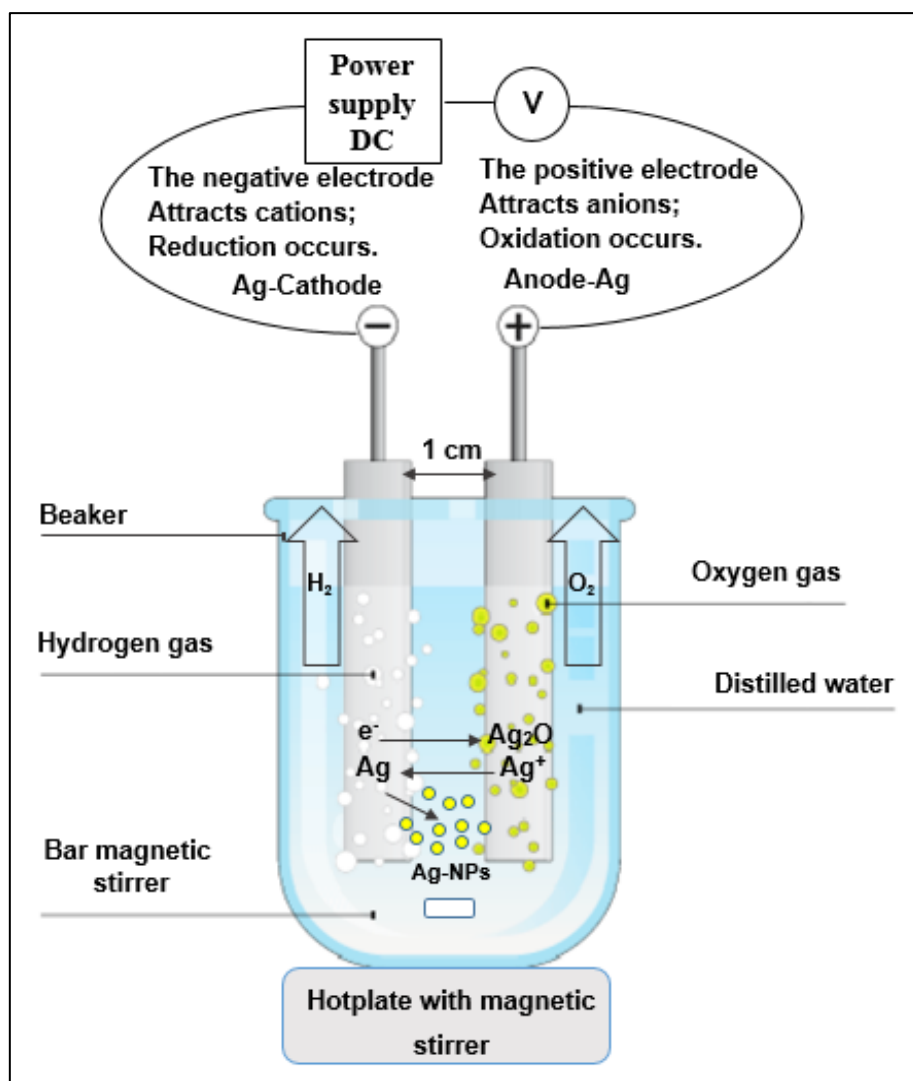
5. Formation of the silver particles via the nucleation and the growth due to Van der vaes attraction.

6. Separation of the silver nanoparticles that has been formed due to the sever steering.

In this process, the regular exchange of D.C current polarity may reduce the rate of deposition of the silver on the cathode. During exchange of polarity, the  $Ag_2O$  formed on the anode before will be hydrated during the interaction with the hydrogen gas:



The duration used for exchanging the polarity was 4 min. below this time, the accumulation of the particles would occur due to the gradual reduction of the efficiency of the surface pole.



**Figure (1) Illustrates scheme of the formation of silver nanoparticles by electrochemical method.**

The silver nanoparticles size was measured using SEM and AFM. Further, molar concentration for the solution was measured by Atomic absorption instrument or a UV-Vis spectrophotometer.

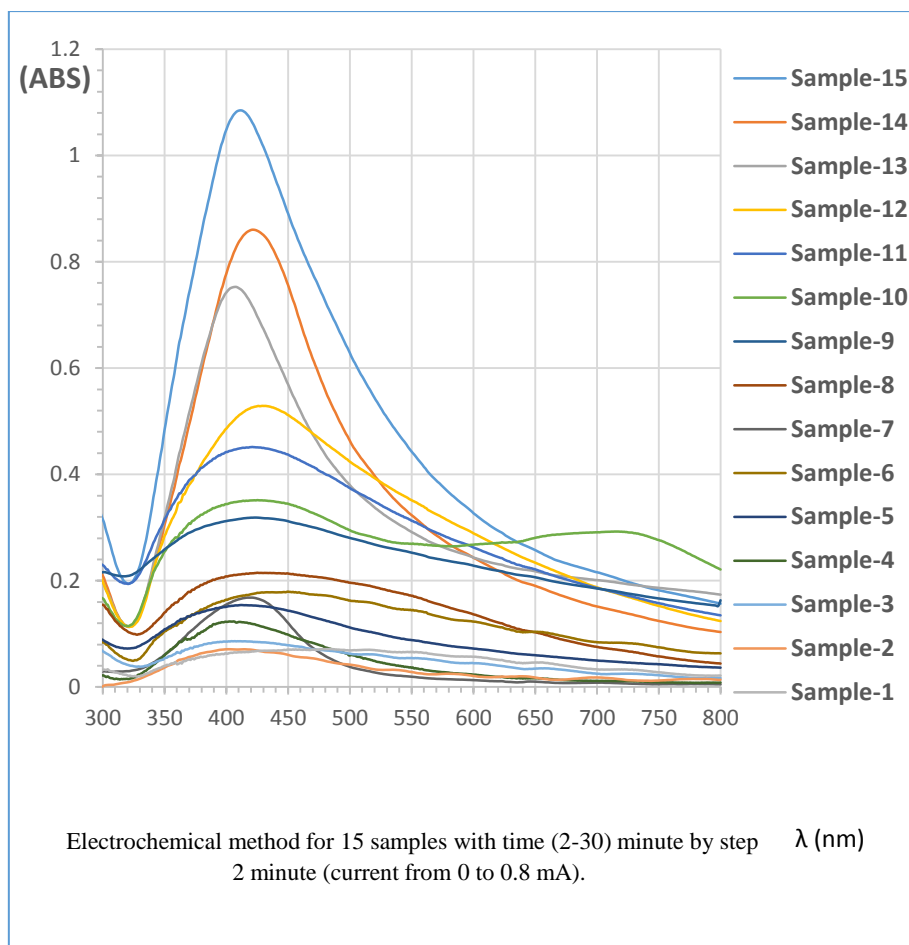
**Result and Discussion**

Table (1) summarizes the properties of the samples used in this work.

**Table (1) Illustrates electrochemical method for 15-samples.**

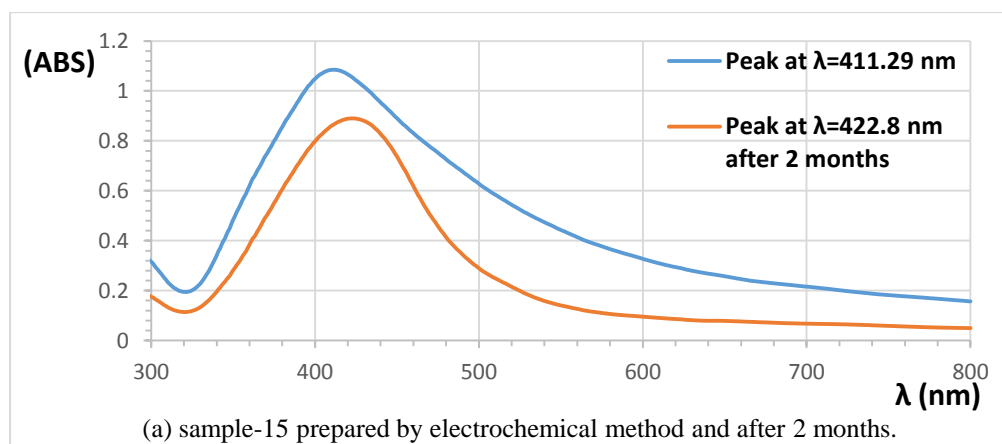
Method Name	Samples	Value of absorption (ABS)	$\lambda$ , nm at Peak of (ABS)
Electrochemical	Sample-1	0.0715	425.36 nm
	Sample-2	0.0725	415.45 nm
	Sample-3	0.0861	409.89 nm
	Sample-4	0.1235	403.25 nm
	Sample-5	0.1544	413.21 nm
	Sample-6	0.1654	420.45 nm
	Sample-7	0.1682	417.22 nm
	Sample-8	0.2149	424.37 nm
	Sample-9	0.3188	423.50 nm
	Sample-10	0.3514	424.37 nm
	Sample-11	0.4511	423.15 nm
	Sample-12	0.5290	429.59 nm
	Sample-13	0.7527	407.27 nm
	Sample-14	0.8601	420.53 nm
	Sample-15	1.0848	411.29 nm

Table (1) shows the absorbance (ABS) as a function of wavelength for 15 samples with different time range (2-30) min step 2 min. It is quite clear that the intensity of peaks has increased due to the increments in the period time of preparation. Because of at least time (current = 0 & impedance very high) there are no any conductivity, but with increase of time with high voltage equal (27-28) V, lead to increased nanoparticles concentrations (increasing the production of the nanoparticles that are suspended in the solution) cause the current growth reach to 0.8 mA and increased of the conductivity as shown in figure (2).



**Figure (2) Shows the ABS as a function of the wavelength for 15 different samples preparation by electrochemical method. Some of the peaks present within the region of longer wavelengths while the other exist within the area of shorter wavelengths.**

Samples-(1, 2 and 3) were tested after longer period (2 months) before doing the UV- Vis spectrum. The results show ABS peaks reduction (concentration has decreased) due to the aggregation of the particles as shown in figure (3)<sub>(a,b,c)</sub>.



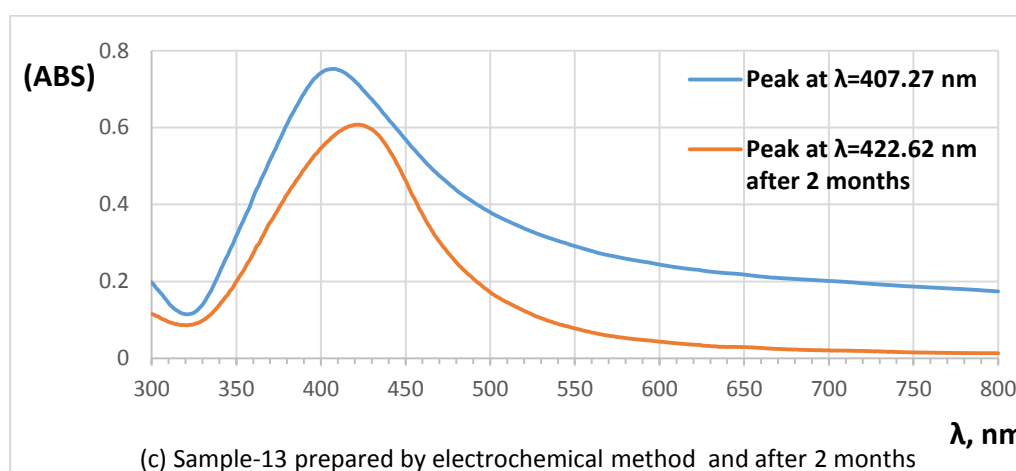
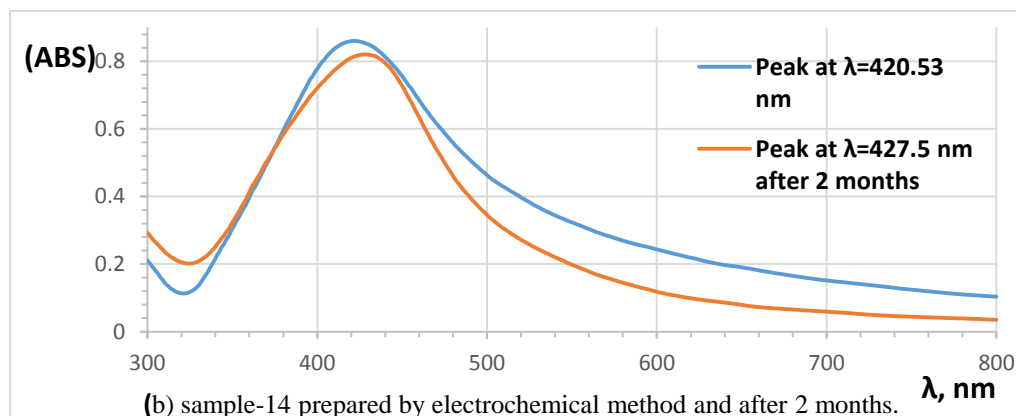
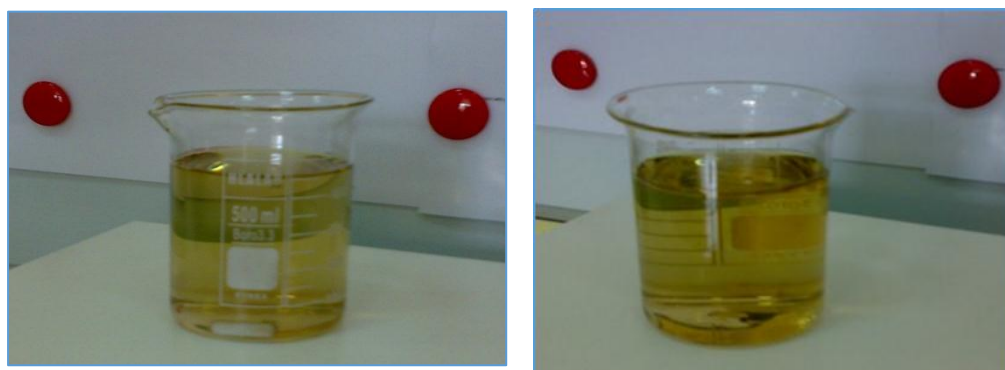
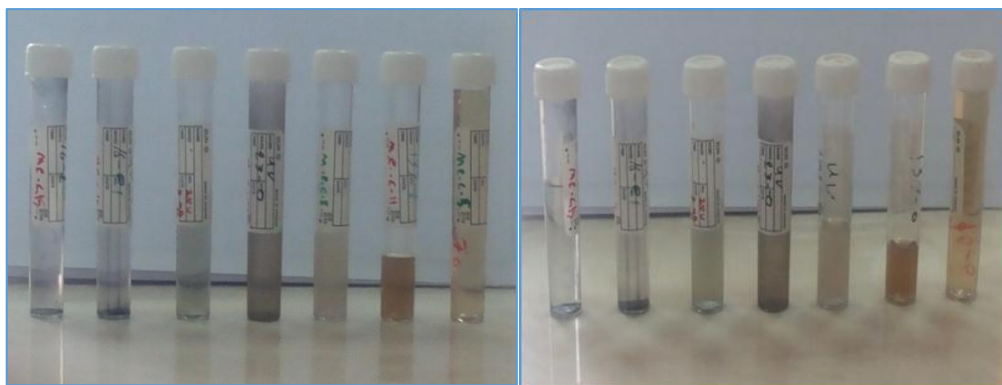


Figure (3) shows absorbance peak for (a) sample-15, (b) sample-14, and (c) sample-13 prepared by electrochemical method and after 2 months shows decrease in absorbance and shift of the peak toward longer wavelengths.

Figure (4) presents the production of the colloidal silver-NPs for different samples in the electrochemical method for different durations of preparation. It is clear that increasing the time of preparation made the color of the solution darker and becomes cloudier due to the aggregation of particles.





**Figure (4): Shows four images for the colloidal silver nanoparticles obtained by electrochemical method for different durations of the preparation.**

It is well known that the quality of electrochemical colloidal silver varies with every batch made. While some of this variance can occur due to mechanical and/or operator malfunction, such as improper voltage due to low batteries. The use of impure waters (other than distilled), incorrect duration of electrode contact, etc. There are other factors which may play an important role in producing high quality of electrochemical silver colloids.

**UV-Vis spectroscopy results:**

The UV-Vis obtained measurements, indicate that through it is possible to predict or estimate the size and the diameter of the nanoparticle size depending on the reference standard measurements as tabulated in table (2).

**Table (2): Shows a comparison between the results of the UV-Vis earned the previous ways and compared with the standard results of previous studies for the expected diameter.**

Method name	Range of $\lambda_{max}$ (nm) at ABS	Typical Range of $\lambda_{max}$ (nm)	Typical Diameter (nm)	Diameter (nm) expected
Electrochemical	403-429	400-410	30	7-30
		405-425	40	10-40
		410-430	50	30-50

**Zeta potential results:**

Table (3) is summarizing the zeta potential measurements of samples in a solution form. For nanoparticles synthesis using different methods, zeta values were measured and found to be -53.18 mV at pH=7.5 for sample-1 (Ag-NPs) prepared by electrochemical method. The value of the zeta potential of method one using citrate coated Ag-NPs provides satisfactory evidence about their little tendency towards aggregation when its negative charges with a diameter of 71.6 nm. This behavior unambiguously suggests the presence of strong electric charges on the particle surfaces to hinder agglomeration. These values are found to fall in the negative side which showed the efficiency of the capping materials in stabilizing the nanoparticles by providing intensive negative charges that keep all the particles away from each other. This result suggests that the Ag-NPs particles and thus their solution is stable

which is also in accordance with the result reported before for colloidal nanoparticles dispersion behavior as shown in figure (5).

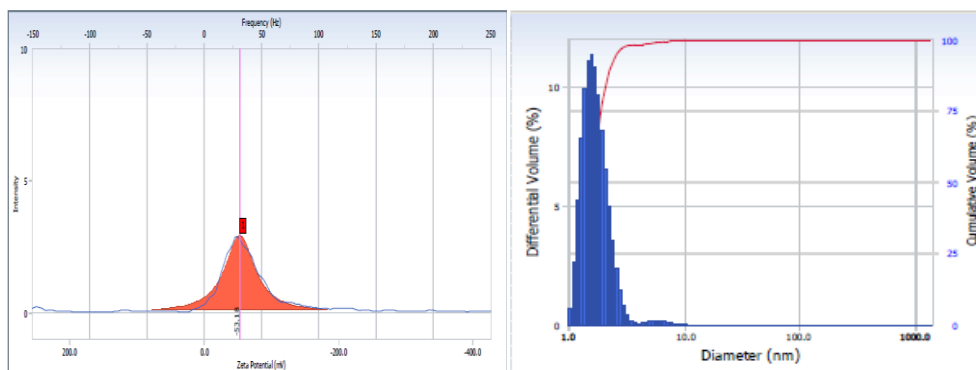
While the value of zeta potential in electrochemical method the Ag-NPs (Sample-2) is positive charge with diameter about 119 nm which indicate that the tendency for aggregation or formation of self-assembled aggregates. Spontaneously, aggregation could have occurred due to frequent collisions between neighboring particles.

This feature for a positive charge of Ag-NPs might be due to the co-existence of dispersed silver ions.  $Ag^+$  is attached on the Ag-NPs and revealed the screening effect of the surface charge as shown in Figure (6).

Measurement Conditions for all samples of colloid silver-NPs are: Temperature: 25.0 (°C), diluent Name: WATER, refractive Index: 1.3328 and viscosity: 0.8878.

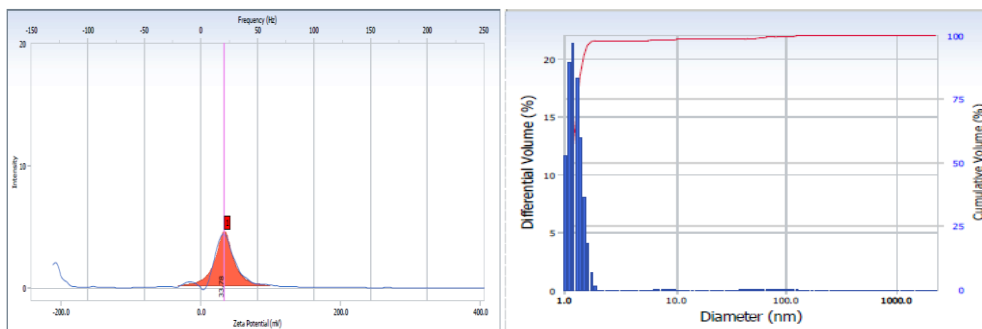
**Table (3): Illustrates Zeta potential Measurements for four samples of colloid silver.**

Sample silver	Mean Diameter (nm)	Diameter (nm)	Zeta Potential (mV)	PH	Mobility (cm <sup>2</sup> /Vs)	Conductivity (mS/cm)	Average Electric Field (V/cm)	Average Currence
Sample -1	1.8	71.6	-53.18	7.5	-4.147 E-004	0.1372	-15.57	-0.11
Sample -2	2.3	119	33.78	7	2.634 E-004	0.0435	16.39	0.04



**Figure (5) (a) Mobility Distribution, (b) Volume Distribution (Diameter= 71.6 nm), for sample-1 of colloidal Ag-NPs obtained by electrochemical method.**

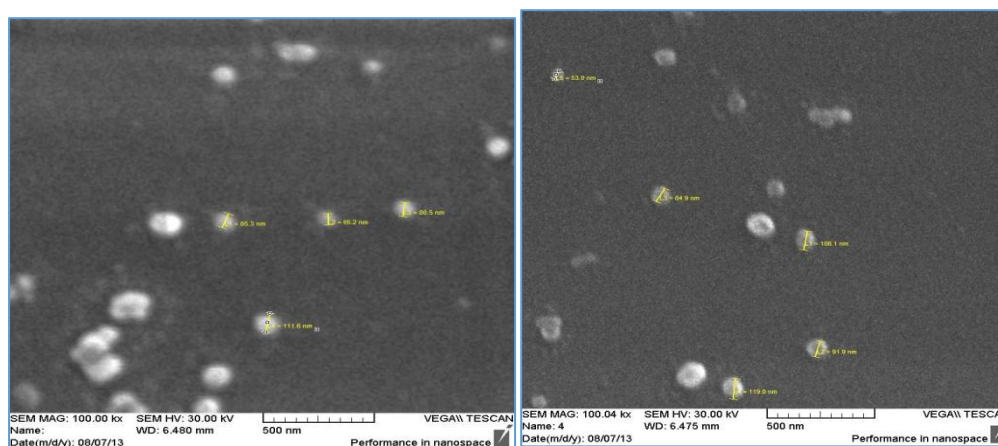




**Figure (6) (a) Mobility Distribution, (b) Volume Distribution (Diameter = 119 nm), for sample-2 of colloidal Ag-NPs obtained by electrochemical method.**

**SEM Measurements:**

To identify the morphology and the structures of the particles in addition to measure the grain size for samples prepared in electrochemical method. Figure (7)[ a, b] shows two SEM images for two samples prepared by electrochemical method.



**Figure (7) SEM image for samples prepared by electrochemical in DDDW.**

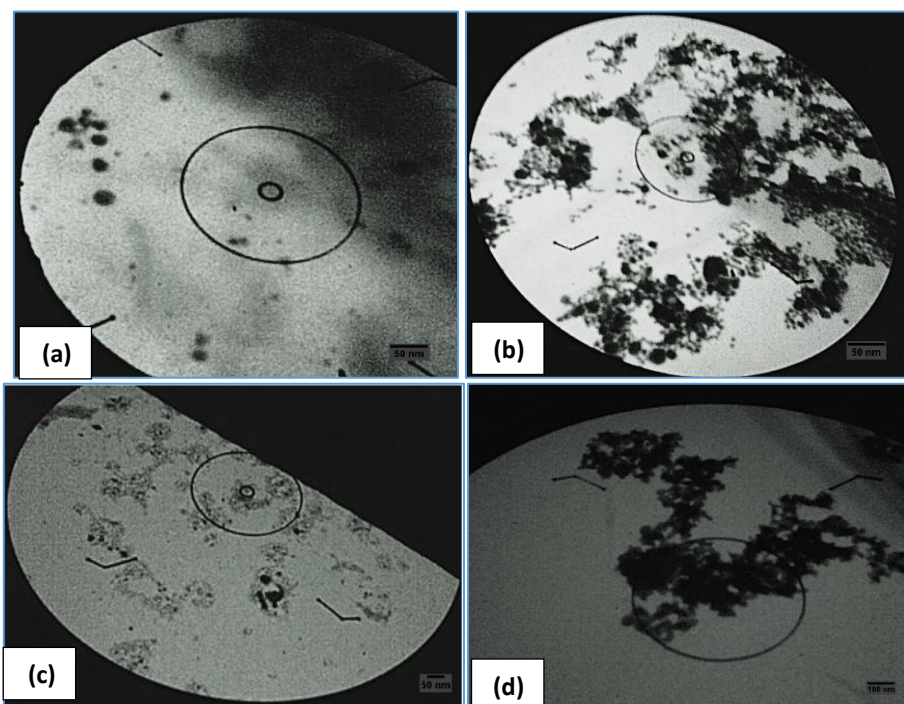
**TEM Measurements:**

Transmission electron microscopy (TEM) investigation of silver nano-composite nanoparticles is a direct and effective approach to determine the particle size and morphology of the nanoparticles, as well as the dispersion uniformity.

Table (4): Size of Silver Nanoparticles Fabricated by Electrochemical Reduction Method.

**Table (4): Size of Silver Nanoparticles Fabricated by Electrochemical Reduction Method by TEM.**

Sample-no.	Figure no.	Magnification	Size, nm
Sample-3	1- (8)a	130 000	10-12
Sample-4	2- (8)b	92 000	15
Sample-8	3- (8)c	92 000	15-20
Sample-13	4- (8)d	92 000	30-44



**Figure (8):** Shows TEM image colloidal silver nanoparticles prepared by electrochemical method. Average size of the particles is (a) (10-12) nm for sample-3, (b) 15 nm for sample-4, (c) (15-20) nm for sample-8, (a) (30-44) nm for sample-13.

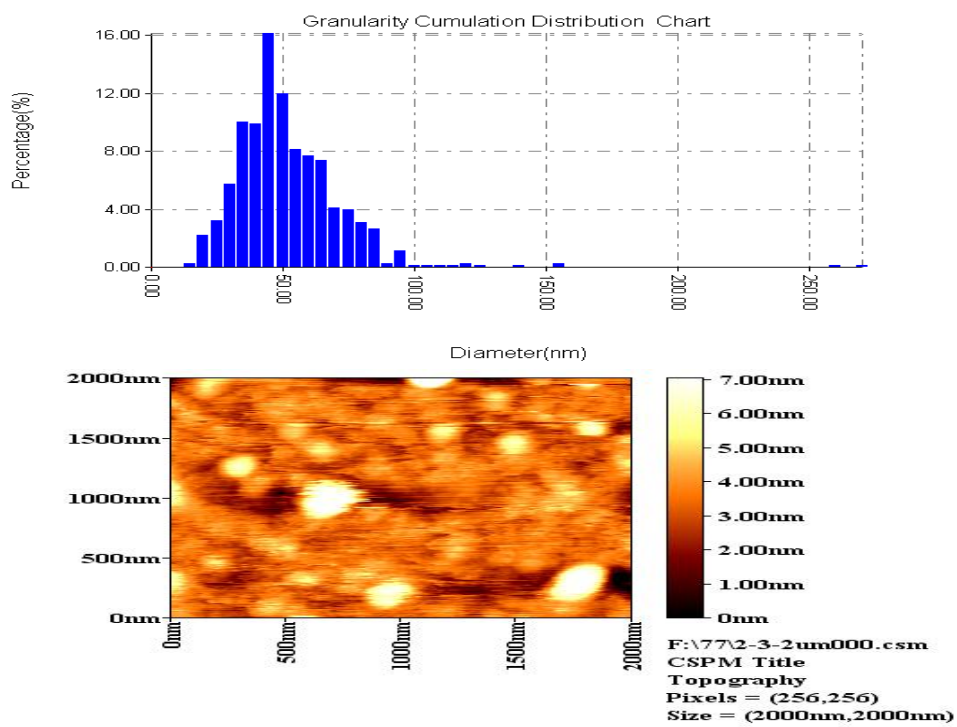
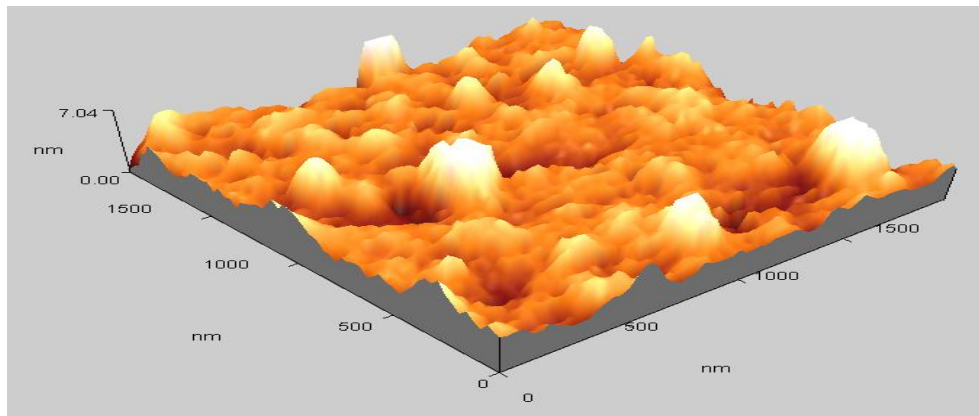
**Surface morphology by AFM Measurements:**

Figures (9) and (10) illustrate the AFM images of Silver nanoparticles prepared by electrochemical method at different currents (0,4, 0,8) mA, the temperature was fixed to be 70 °C.

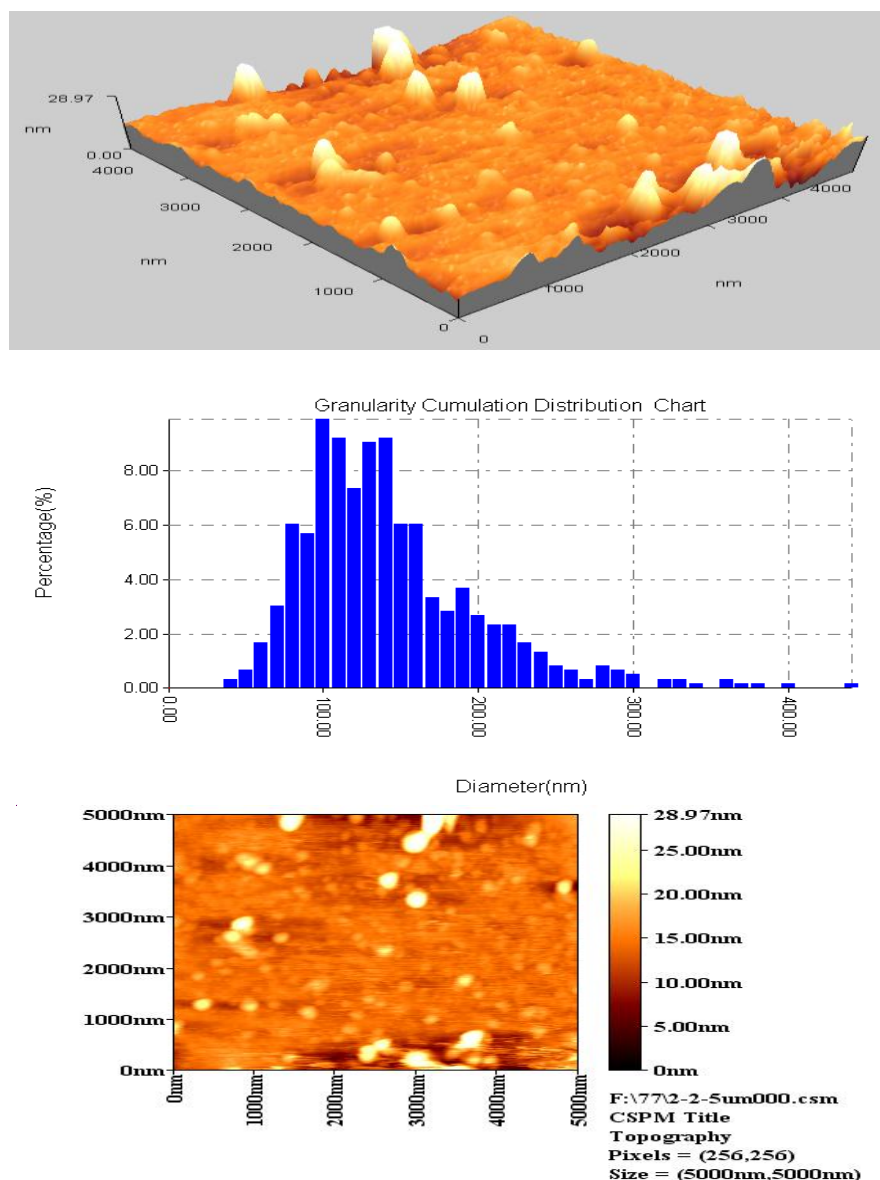
Table (5) represents the values of RMS and main grain size taken from the AFM images results from electrochemical method.

**Table (5):** AFM characterizations of the Ag-NPs prepared by electrochemical method at different currents.

Figure no.	Current, mA	RMS, nm	Main grain size, nm
(10)	0.4	7.0	50
(11)	0.8	28.27	180



**Figure (9) Shows the 3D image of the AFM for silver-NPs film prepared by electrochemical method at current=0.4 mA, the attached images for histogram and the 2D images examined by AFM.**



**Figure (10) Shows the 3D image of the AFM for silver-NPs film prepared by electrochemical method at current=0.8 mA, the attached images for histogram and the 2D images examined by AFM.**

### Conclusion

Among many methods of preparing silver ion-NPs; such as pulsed laser ablation and chemical synthesis, electrochemical method was found to give the optimum results. The present method is simple, fast, low cost and can produce large quantities. In addition, the production of the silver NPs prepared by electrochemical method is more pure and would be suitable for medical applications.

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