

## Spectral Study of Silver Nanoparticles Prepared by Chemical Method

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### ABSTRACT

Silver nanoparticles were prepared by the reduction of silver salt (silver nitrate  $\text{AgNO}_3$ ) solution using three different methods. The main differences between these methods is by belong to the reducing agent. It is found that the prepared silver nanoparticle was pure and stable for long time. UV-VIS spectrometry indicated formation of spherical silver nano particles. The surface plasmon resonance peaks in absorption spectra for silver colloidal solution showed that the absorption maximum range was at 380- 420 nm. The structures are confirmed by X-ray diffraction (XRD) and the crystallite size was determined from X-ray line broadening using the Scherrer's equation and it was about 32 nm. AFM measurements show that silver nano particles have the average diameter of 69.39 nm and 81.91 nm.

### الدراسة الطيفية لدقائق الفضة النانوية المحضرة بالطريقة الكيميائية

#### الخلاصة

تم تحضير دقائق الفضة النانوية باستخدام ثلاثة طرق مختلفة وذلك باختزال نترات الفضة ( $\text{AgNO}_3$ ). إن الاختلاف الرئيسي بين هذه الطرق هو استخدام العامل المختزل. دقائق الفضة النانوية المحضرة وجدت نقية ومستقرة لوقت الطويل. جهاز قياس الطيف أشار إلى تشكيل الدقائق النانوية الفضية الكروية. قُمت طيف الامتصاص للمحلول الفضي أظهرت بأن الإمتصاص الأعظم كان في مدى (380 - 420 nm). التركيب لدقائق الفضة النانوية والحجم البلوري مؤكدة بواسطة قياس حيود الأشعة السينية (XRD) و بإستعمال معادلة Scherrer's كان حوالي 32nm.

### INTRODUCTION

Colloidal particles are increasingly receiving attention as important starting points for the generation of micro and nano structures [1]. These particles are under active research because they possess interesting physical properties differing considerably from that of the bulk phase. It comes from small sizes and high surface/volume ratio [2]. Silver nano particles 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],  $\gamma$ -radiation [4] photochemical [5], laser ablation

[6] etc. The most popular preparation of Ag colloids is chemical reduction of silver salts by sodium borohydride, sodium citrate and cetyltrimethylammonium bromide, (CTAB). 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 [7]. 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. Silver nanoparticles exhibit new optical properties, which are observed neither in molecules nor in bulk metals. One example is presence of absorption band in visible light region. This band appears due to the surface Plasmon oscillation modes of conduction electrons which are coupled through the surface to external electromagnetic fields [8]. The surface plasmon resonance and large effective scattering cross section of individual silver nanoparticles make them ideal candidates for molecular labeling, where phenomena such as surface enhanced Raman scattering (SERS) can be exploited [9]. In addition, silver nanoparticles have recently been shown to be a promising microbial material [10]. In this research, Ag nanoparticles were synthesized by silver salt (AgNO<sub>3</sub>) reduction with sodium citrate, sodium borohydride and cetyltrimethylammonium bromide (CTAB).

## EXPERIMENTAL

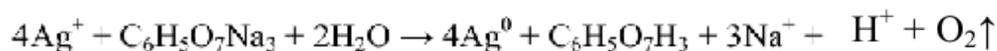
### Preparation of Ag colloid

#### Silver nitrate with trisodium citrate

The materials used in this method silver nitrate (AgNO<sub>3</sub>) and trisodium citrate (TSC) (C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>Na<sub>3</sub>) of analytical grade purity. The silver colloid was prepared by using chemical reduction method according to the description of Lee and Meisel [11].

All solutions of reacting materials were prepared in distilled and deionized water (DW). In a typical experiment 25 ml of 0.01g (AgNO<sub>3</sub>) was heated to boiling. To this solution 20 ml of 0.025 g trisodium citrate was added drop wise. The solution was mixed vigorously, heated until color's change is evident (pale yellow). Then the solution was cooled to room temperature while it is stirring. The Ag nanoparticles prepared by this method have low stability for short time.

The chemical for such reduction can be written as follows:



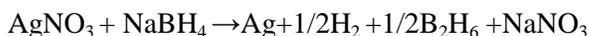
#### Silver nitrate with oxalic acid

Colloidal Ag nanoparticles were prepared by reducing silver nitrate with oxalic acid in presence of (CTAB). Three solutions were prepared. First dissolve 0.01 g of AgNO<sub>3</sub> in 5ml DW second, dissolve 0.01 g of CTAB in 10 ml of DW third, and dissolve 0.05 g of oxalic acid in 10mlDW. The solution of CTAB was added dropwise to the solution of nitrate. After that dropwise the oxalic acid solution to the results of CTAB and nitrate. After mixing oxalic solution, the color result to change light acorned followed that, the color change to dark acorned. Finally, the color of the result solution become yellow.

### Silver nitrate with sodiumborohydride

This method based on mixing silver nitrate with ( $\text{NaBH}_4$ ). Firstly dissolving 0.0001 g of  $\text{AgNO}_3$  in 5 ml of DW and 0.0006 g of  $\text{NaBH}_4$  in 5ml DW. The solution of  $\text{NaBH}_4$  become light yellow after dropwise of  $\text{AgNO}_3$  solution with storing stirring. If the stirring is continued once all the silver nitrate has been added, aggregation is likely to occur, the yellow darkens, turns violet.

The chemical equation for this method can be written as follows:



### characterizations of NPs

-Absorbance spectra (SPE spectra) of NPs solution were measured by UV-VIS double beam spectrophotometers, CECIL C. 7200 (France) and SHIMADZU. All spectra were measured at room-temperature in a quartz cell with 1 cm optical path.

The Agnanoparticles samples were studied by X-ray diffraction technique (Philips PAN analytical, The Netherland) using  $\text{Cu K}\alpha$  radiation. The measure condition X-ray target Cu, wavelength 15.406 (nm), generator voltage and current was set at 40 KV and 30 mA respectively. The Ag nanoparticles samples were scanned in the  $2\theta$  range 20 to 70 (deg) ranges in continuous scan mode. The scan rate was 5 deg /sec.

The AFM analysis was done using scanning prop microscopy (CSPM-3000). It is an instrument capable of measuring the topography of a given sample. A nanosized tip attached on a cantilever is traded over the sample and a 3D image of the sample topography is generated on a computer.

## RESULTS AND DISCUSSIONS

### UV-VIS spectroscopy analyses

Figure (1) Shows UV-VIS spectroscopy of Ag nanoparticles produced using mixing  $\text{AgNO}_3$  and TSC. Which indicates that the surface plasmon resonance peak was broad and located between 350 to 720 nm with an absorption maximum at 450 nm. Comparison of the experimental results with reference results [12] which showed the diameter range of AgNPs in colloidal solution is between 75 and 110 nm.

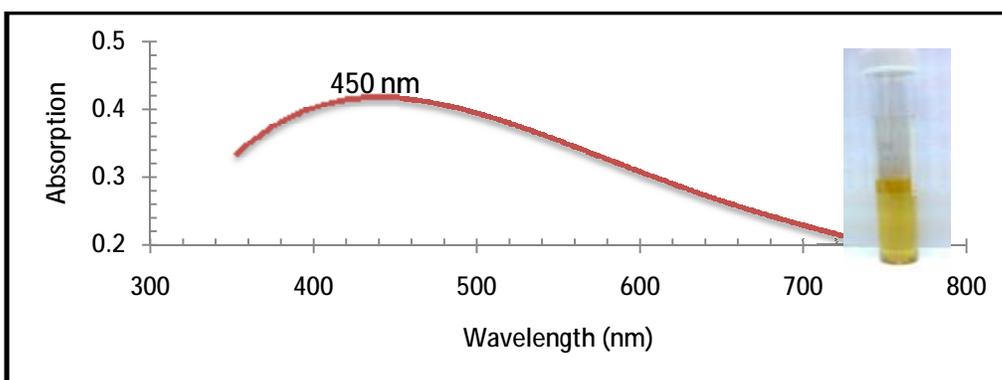


Figure (1) UV-VIS spectral and photo of Ag nanoparticles by chemical reduction  $\text{AgNO}_3$  with TSC.

Figure (2) shows the color of colloidal Ag nanoparticles product using of  $\text{AgNO}_3$  with CTAB and oxalic acid. Figure (2). Depicts 4 color belong to colloidal Ag nanoparticles with time of storage. It can be concluded that, the reducing  $\text{AgNO}_3$  used in this method was slow, therefore, the reaction needs to more time to complete. The reducing agent reduces large Ag nanoparticles to form small Ag nanoparticles after period of time.



Figure (2) photo shows formation stages Ag nanoparticles prepared by  $\text{AgNO}_3$  with CTAB with oxalic acid.

Figure (3) represents the UV-VIS spectroscopy of colloidal Ag nanoparticles produced  $\text{AgNO}_3$ , CTAB, and oxalic acid. The peak of surface Plasmon resonance appears at 407 nm with peak width half maximum (PWHM) at 95 nm. After that the peak of SPR be broaden. The increase of peak height indicates increases of Ag nanoparticles concentration. The Ag nanoparticles prepared in this method have high stability with long time.

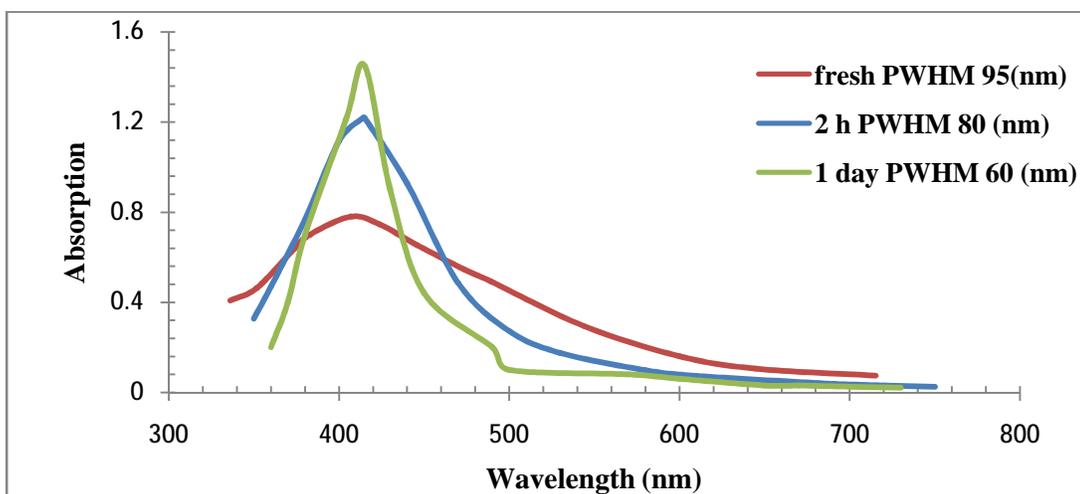


Figure (3) UV-visible spectra of formation stages Ag nanoparticles prepared by  $\text{AgNO}_3$  with CTAB with oxalic acid.

Figure (4) Shows that the UV-VIS spectroscopy colloidal AgNPs using  $\text{AgNO}_3$ ,  $\text{NaBH}_4$ . The preparation of Ag nanoparticles have low stable for short time, because the drawbacks to this synthesis were that the sodium borohydride was unstable. The nanoparticles will be aggregated, although this can be avoided by capping the nanoparticles with some stabilizing agent such as polyvinyl alcohol. The surface Plasmon resonance peak absorption maximum at 386.6 nm as show in Figure (4).

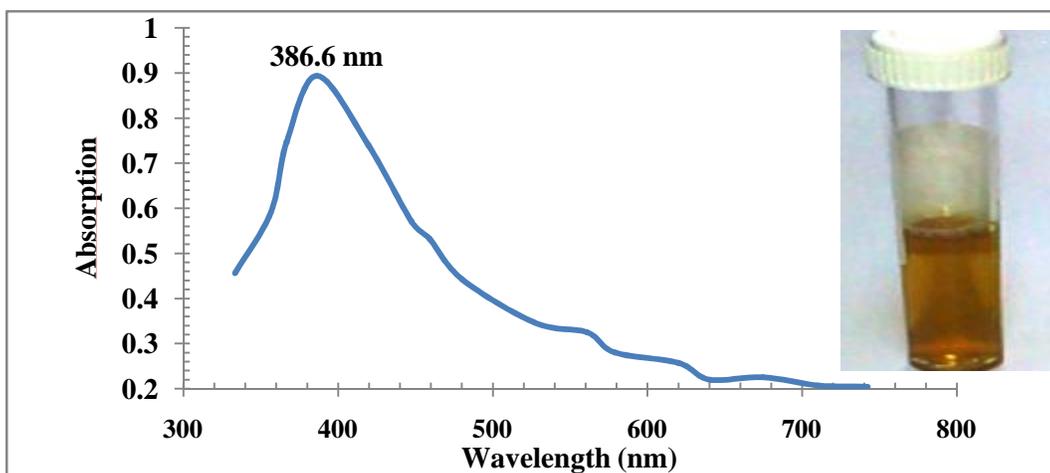


Figure (4) UV-VIS spectral and photo of yellow Ag nanoparticles was produced by chemical reduction of  $\text{AgNO}_3$  with  $\text{NaBH}_4$ .

#### X-RAY Diffraction analyses

Figure (5) Shows a typical X-ray diffraction (XRD) of the colloidal Ag nanoparticles prepared by using  $\text{NaBH}_4$  as a reducer. The reflection peak can be indexed to face-centered cubic silver. The lattice constant ( $a$ ) calculated from this pattern is  $4.085^\circ\text{A}$ , which is consistent with the standard value of  $4.085^\circ\text{A}$  (JCPDS Card File 04-0783). No impurities are detected from this pattern. This indicates that pure silver metal is obtained under the present synthetic conditions. The crystallite size of the silver nanoparticles equal 32 nm. It was determined from X-ray line broadening using the Scherrer's equation.

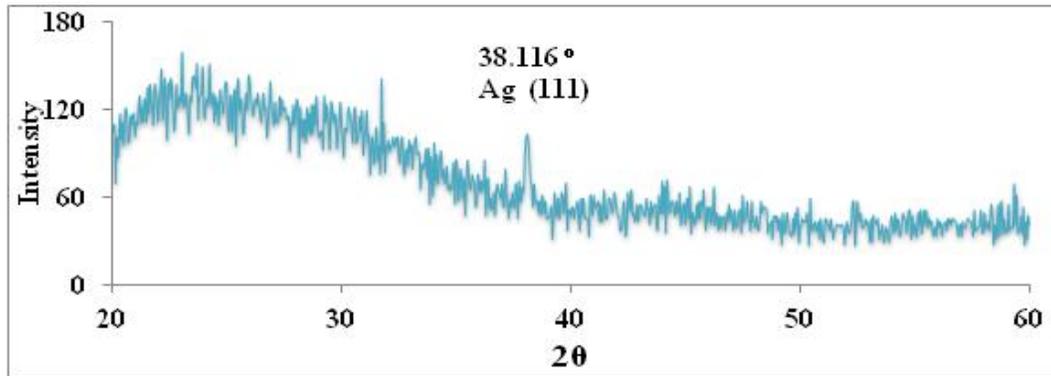


Figure (5) X-Ray diffraction of Ag nanoparticles was produced by chemical reduction  $\text{AgNO}_3$  with  $\text{NaBH}_4$ .

**Atomic Force Microscope (AFM) analyses**

Figure (6) Shows AFM images and corresponding size distributions of Ag nanoparticles were prepared by reducing  $\text{AgNO}_3$  by (CTAB) in presence of oxalic acid. The Ag nanoparticles were storage at room temperature for eight months before carrying out AFM measurement, without addition of any stabilizer agent. The nanoparticles thus prepared were calculated to have the average diameter of 69.39 nm.

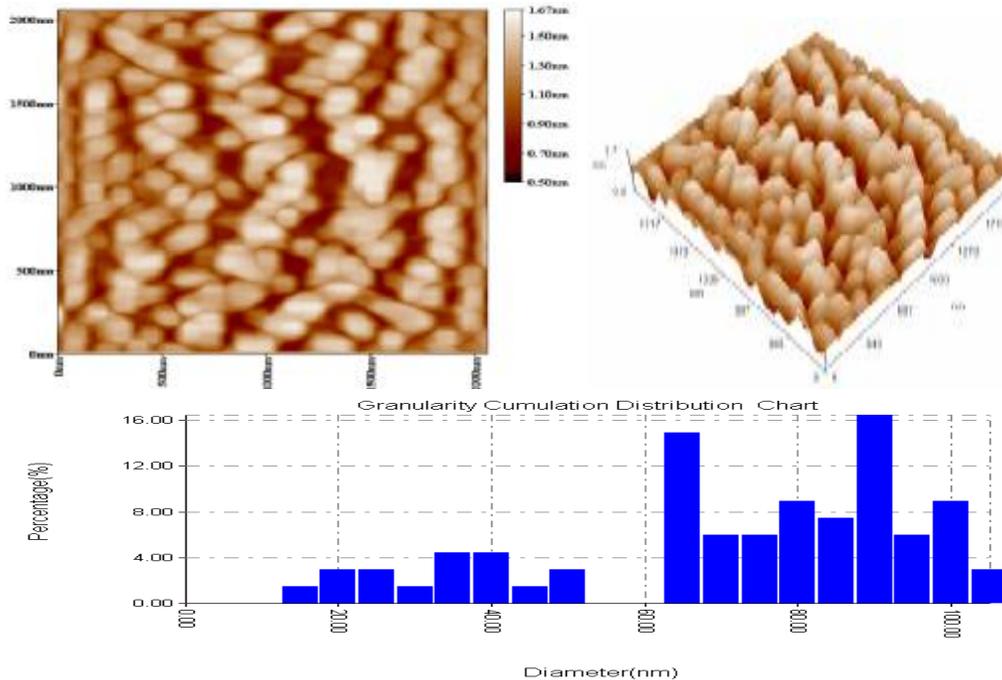
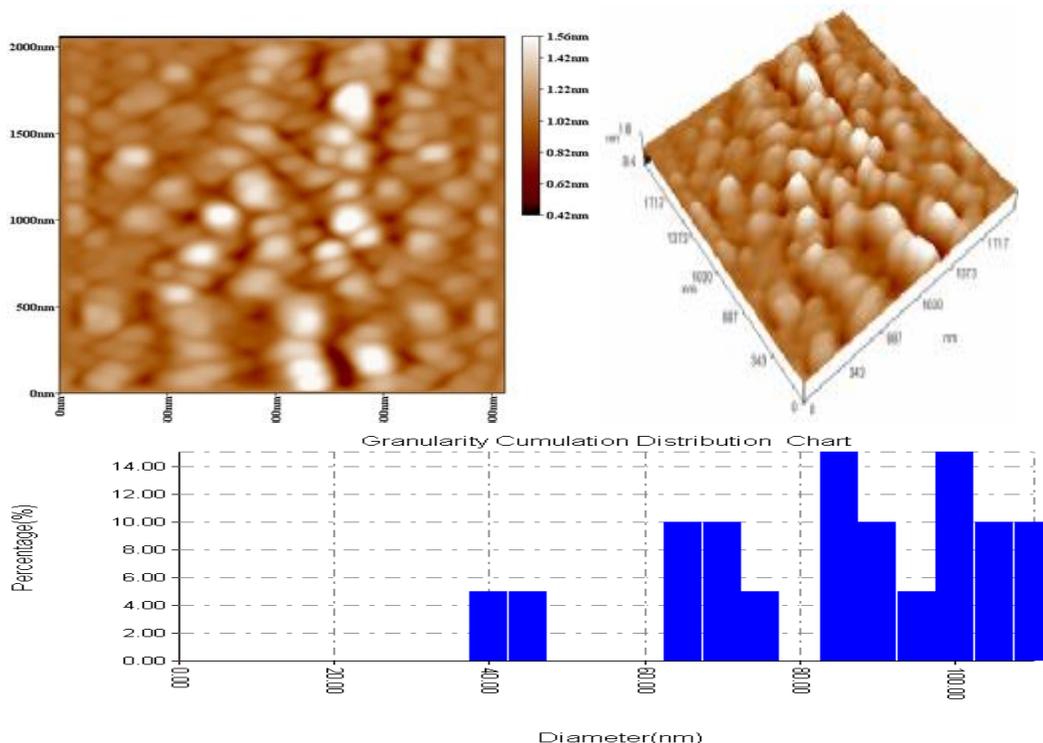


Figure (6) Shows AFM images and size distributions of AgNPs were prepared by reducing silver nitrate with (CTAB) in presence oxalic acid.

Figure (7) Shows AFM images and corresponding size distributions of Ag nanoparticles were prepared by reducing  $\text{AgNO}_3$  with  $\text{NaBH}_4$ . The silver nanoparticles were storage at room temperature for eight months before carrying out AFM measurement, without addition of any stabilizer agent. The nanoparticles thus prepared were calculated to have the average diameter of 81.91nm.



**Figure (7) Shows AFM images and size distributions of AgNPs were Prepared by reducing  $\text{AgNO}_3$  with  $\text{NaBH}_4$ .**

## CONCLUSIONS

The colloidal Ag nanoparticles prepared using three different method depends on the change of reducing agent (TSC, CTAB and  $\text{NaBH}_4$ ) with  $\text{AgNO}_3$ . On the other hand, the effect of oxalic acid are studied on the formation of Ag nanoparticles by UV-VIS spectroscopy result. UV-VIS spectroscopy indicated formation of spherical silver nanoparticles. The surface plasmon resonance peaks in absorption spectra for silver colloidal solution showed that the absorption maximum range was at 380- 420 nm. X-ray measurements have shown that the crystallite size of the AgNPs equal 32 nm. It was determined from X-ray line broadening using the Scherrer's equation. AFM measurements show that AgNPs have the average diameter of 69.39 nm and 81.91 nm and tend to form aggregates.

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