

## Synthesis and Characterization of Gold Nanoparticles Colloids

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**Abstract:** Gold nanoparticles (Au Nps) were characterized by superior opto-electronic properties due to their unique interaction with incident light. In the presence of the oscillating electromagnetic field of light, the conduction band electrons of metal nanoparticles undergo collective oscillations in resonance with the frequency of light, which is called Surface Plasmon Resonance (SPR). Gold nanoparticles colloids, prepared using citrate reduced method (Turkevich method), were exposed beside its original state to different external factors like ultrasonic dispersion, centrifugation and nylon membrane separation. The different resulted solutions were characterized using UV-VIS spectrophotometer for optical properties determination, scanning electron microscope (SEM) for microstructural investigation and atomic force microscope (AFM) for particle size and interparticle distance determination. Good correlation between UV-VIS spectroscopy, SEM and AFM was obtained that explained the parameters affecting particle size, state of dispersion and the stability of the prepared gold nanoparticles colloids.

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**Key Words:** Gold nanoparticles colloids; Turkevich method; Synthesis of gold nanoparticle; stability.

### 1. Introduction

Metal nanoparticles such as gold (Au) and silver (Ag) synthesis have been studied intensively over the last few years due to their wide applications in chemistry, physics and biology [1-4]. Gold nanoparticles are of particular interest because of its enhanced optical, electrical and photothermal properties [1-4]. So, gold nanoparticles have potential application in non-linear optics, electronics, catalysis, clinical medicine, analytical chemistry and have been used as probes in mass spectroscopy [1-2].

Owing to its extra properties and wide applications in all fields, gold nanoparticles are considered as the key material and building block in future [4].

The electronic properties of gold nanoparticles have received a considerable interest in electronic and opto-electronic devices [5]. Where, the intriguing optical properties of gold nanoparticles, as reflected by their intense color, are attributed to their unique interaction with incident light [6-10]. In the presence of the oscillating electromagnetic field of light, the conduction band electrons of metal nanoparticles undergo collective oscillations in resonance with the frequency of light, which is called Surface Plasmon Resonance (SPR) [6-10]. These oscillations induce charge separation between the free electrons and the ionic metal core, which exerts a restoring Coulomb force to make the electrons oscillate back and forth on the particle surface resulting in dipole oscillation in the simplest case. SPR oscillation induces a strong

absorption of light which is the origin for the observed colors of the colloidal solution as explained by Mie Theory [6].

Gold Nanostructure colloids have been developed using physical and chemical approaches [4]. The chemical approach produces nanomaterial through simpler and economical chemical routes characterized by the ease synthesis modification as well as the size and shape control [4] while the physical approach necessitates the use of sophisticated equipments that are expensive [4].

It was found that size, shape and surface morphology play a vital role in controlling the physical, chemical, optical and electronic properties of these nanomaterials [11]. So, selective synthesis of such nanomaterials remains a significant challenge [11]. Preparation of metal nanoparticles involves the reduction of metal ions in solution, one of the famous methods used in gold nano colloids synthesis is Turkevich method [12-14] that is based on nucleation, growth and agglomeration where nano metal ions in solution are characterized by high surface energy making them very reactive and undergo aggregation [12-14]. So, colloidal solution requires protective agents for electrostatic and steric stabilization and to prevent agglomeration [15].

The use of protective agent offers electrostatic stabilization through coulombic repulsion between the particles caused by the electrical double layer formed by capping agent ions adsorbed on the particle surface and the corresponding counter ions.

Also it acts as a protective shield on the metallic surface, so steric stabilization is achieved. In this way nanometallic cores are separated from each other and agglomeration is prevented [15].

In this paper, gold nanoparticle colloids were prepared using citrate reduced method (Turkevich method). The particle size distribution, interparticle distance and stability of gold nanoparticles pretreated under different conditions were performed in order to make correlation between the parameters affecting particle size, state of dispersion and the stability of the prepared gold nanoparticle colloids.

## 2. Experimental

### 2.1. Materials

Gold sodium chloride (99.5%, Suvchem), Trisodium citrate dehydrate (99.9%, Winlab), Ultrapure water (Millipore water). All glasswares were thoroughly cleaned with aqua regia (Conc. HCl: Conc. HNO<sub>3</sub>) (3:1) prior to the preparation.

### 2.2. Synthesis of gold nanoparticle colloids using Turkevich method.

50 ml of aqueous gold salt (19.7 mg, 1.0 mM) was heated until boiling with vigorous stirring using a magnet stirrer for 15 min then 5 ml of aqueous tri sodium citrate (57.04, 38.8 mM) was added rapidly. It is to be noted that tri sodium citrate acted as a capping and reducing agent under heating condition [16]. Otherwise, it acted only as a capping agent when used at room temperature. The preparation procedure was performed under reflux to maintain a constant volume [5]. Color change was observed within the first minute of tri sodium citrate addition from yellow, colorless, black to finally purple color indicating nanoparticles formation [17] the solution was boiled with vigorous stirring for a further 15 min and allowed to cool to room temperature. The resulting gold nanoparticles colloids were subdivided into 4 parts as given in Table 1. Beside its original state, the three other solutions were exposed to ultrasonic dispersion for 15 min, centrifuge force where the supernatant solution was obtained from the parent colloidal solution that was centrifuged at 4000 rpm for 10 min using (Hermele-Z300) and finally permeate solution that resulted from the filtration of the parent colloidal solution through a nylon membrane.

**Table 1. Pretreatment and abbreviation of gold nanoparticles colloids.**

Pretreatment	as prepared	Ultrasonicated for 15 min.	Centrifuged at (4000rpm) for 10 min.	Passed through nylon membrane
Sample	Au21	Au22	Au24	Au25

## 2.3. Gold nanoparticles colloids characterization

### 2.3.1 Ultraviolet-Visible Spectrophotometry

Ultraviolet-Visible (UV-VIS) spectrophotometer (Cole Parmer 2100 UV) model was used to study the optical behavior of gold nanoparticles colloids. The different samples were placed in 1.5 ml cavity sorted cuvettes at room temperature and the spectra were measured over wavelengths from 320 to 650 nm (double distilled 18 MΩ) water is used as a reference material.

### 2.3.2 Low-Temperature Low-Vacuum Scanning Electron Microscopy

Low Vacuum Scanning Electron Microscope (LV-SEM) (JEOL JSM -5600-LV) model was used to investigate the structure and average particle size of the formed gold nanoparticles colloids. A drop of each colloid was frozen and placed on a grid to be imaged. This is a new freezing technique that is developed for serving in the dynamic examination of micro spherical solid particles in doubled distilled water in connection with (LV-SEM). [18]

In the present work the above technique is used to observe gold nanoparticles colloids in which, a special cryostat stage is needed to keep the specimen temperature between -100 to -50 °C inside the Low Temperature LT-LV-SEM. In this temperature range the liquid sample was kept in a frozen state at low vacuum according to the water temperature pressure curve in figure (1.a).

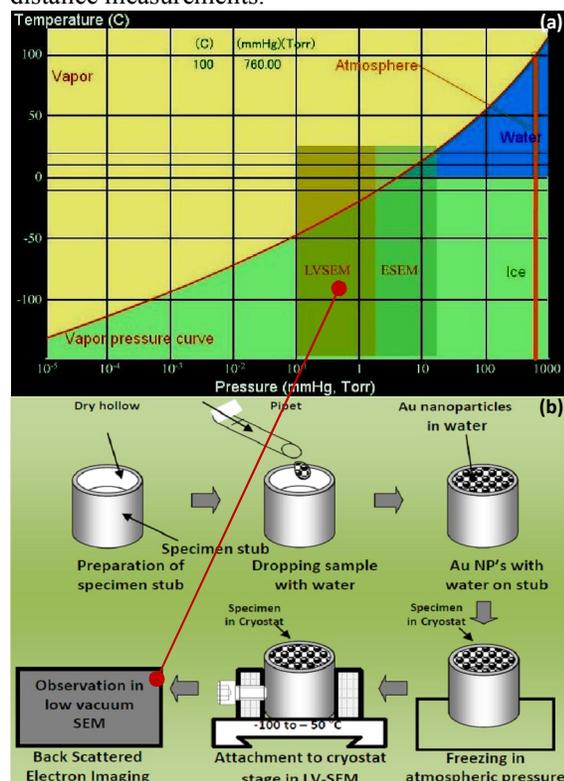
According to this temperature pressure curve, if the frozen liquid specimen temperature rises over -50 °C inside the LT-LV-SEM two possibilities may occur, sublimation or sample returning to liquid state again inside vacuum. To prevent these possibilities the time, in which the range of temperature between -100 to -50 °C, must be increased to cover all the needed investigations for the frozen specimen.

Au nanoparticles colloids droplets were suspended in water then frozen in atmospheric pressure at -100 °C by the method illustrated in figure (1.b). The frozen specimen was quickly transferred onto the cryostat specimen stage in the LT-LV-SEM and then evacuated. Back scattered electron micrographs were taken by the LT-LV-SEM. During the observations the temperature of the cryostat specimen stage increases slowly with time from -100 to -50 °C [19]. All these observations were recorded before the temperature reaches the critical line and the liquid sublimated in the low-vacuum. The different LT-LV-SEM backscattered micrographs in the nanoscale range were obtained at an acceleration voltage of 30 KV and a higher magnification scale.

### 2.3.3 Atomic Force Microscopy

Atomic Force Microscope (AFM) was used for determining the average particle size, microstructure

investigation with higher resolution and interparticle distance measurements.



**Figure (1): (a) Water temperature pressure curve, (b) Low-vacuum SEM freeze method for gold nanoparticles colloids observation.**

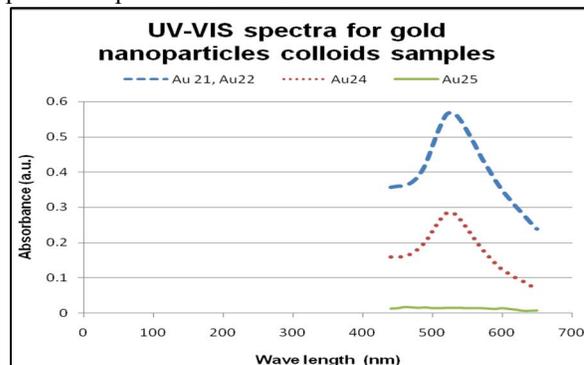
### 3. Results and Discussion

#### 3.1. UV-VIS Absorption Spectrophotometry

UV-VIS spectra of gold nanoparticles colloids were measured after 48 hours reaction time following the preparation. Strong light absorption in the visible region at a wavelength of 530 nm was obtained for the samples Au21, Au22 and Au24, as given in figure 2. The strong absorption band results from nanoparticles coherent oscillations of the free electrons on the particle surface due to their interaction with light called the Surface Plasmon Resonance (SPR) effect as outlined before [6-10].

The decrease of the peak height of absorption band, full width at half maximum (FWHM), of sample Au24 could be attributed to the surface plasmon absorption of low percentage of spherical nanoparticle present in this sample [20]. This decrease was due to the centrifuge effect where higher percent of nanoparticles were collected as precipitate at the tube wall leaving lower percent of nanoparticles in the supernatant solution (Au24) as well as the slight decrease in the average particle size of Au24 [21] as observed in Figure 3 (b).

No absorption spectra was observed for sample Au25, this was due to one of these two reasons: the first one was the separation of Au nanoparticles at the nylon membrane surface leaving permeate solution without Au nanoparticles and consequently no absorption spectrum was observed. The second one was the separation of larger nanoparticles at the nylon membrane surface leaving very small particles < 3nm in the permeate solution. So in this case, there is no SPR feature for such small Au nanoparticles [22]. The first reason is almost happened in the present experimental condition.



**Figure 2. UV-VIS spectra for different pretreated gold nanoparticles colloids: Au21, Au22, Au24 and Au25 samples.**

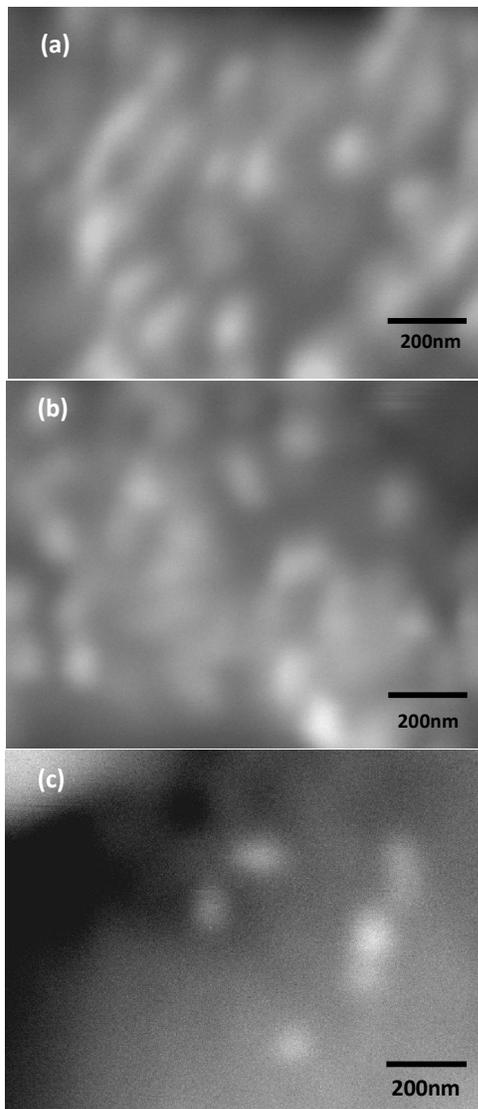
#### 3.2. LV-SEM Imaging

Digital Imaging Processing (DIP) in conjunction with SEM particle counting method was applied to calculate the size of the formed Au nanoparticles colloids [23] [24]. Figure 3 shows SEM micrographs of Au21, Au22 and Au24 samples respectively. Spherical nanoparticles with an average size of 30 nm were observed with Au21, Au22 samples as observed in figure 3 (a) respectively. Slight decrease in the average particle size to 28 nm for sample (Au24) was observed may be due to the separation of small and large nanoparticles by centrifugation, as shown in figure 3 (b). SEM micrographs of the Au21, Au22 samples showed higher density of dispersed nanoparticles and aggregated spherical nanoparticles in the form of raspberry type morphology [25]. On the other hand Au24 sample was characterized by lower density of the dispersed and aggregated nanoparticles when compared to Au21 and Au22 samples. This result could be the reason of lower intensity of SPR band as shown in figure 2.

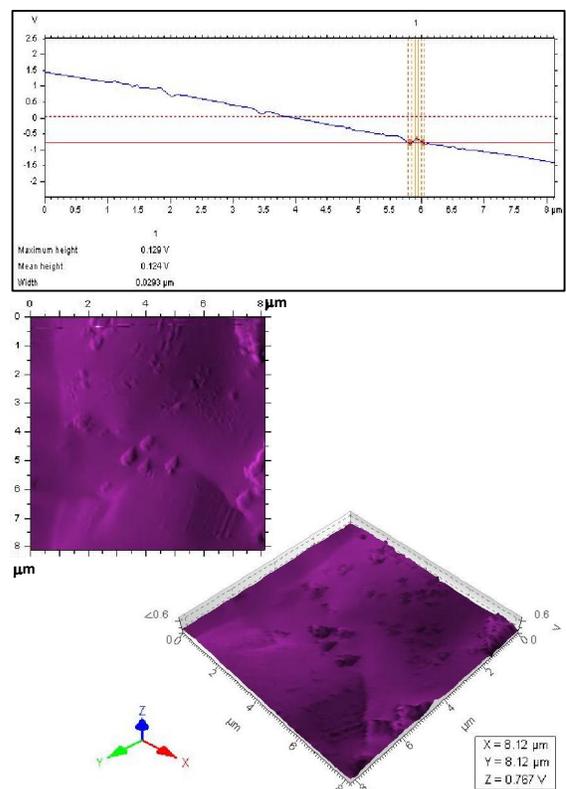
#### 3.3. AFM Analysis

Nanoparticles morphology was studied using Atomic Force Microscopy (AFM) for Au24 nanoparticles sample with an average size (29.3 nm) as shown in figure 4. Low degree of aggregation was observed as correlated with SEM results, Figure 3.

shows also, lower nanoparticles density which confirmed the decrease in the peak intensity of the UV-VIS spectrum of Au24 sample as given in figure 2. It is noted that the interparticle distance was one of the important keys parameters on the proof of non-aggregation of the particles where larger interparticle distance showed higher stability against agglomeration and longer life-time [26]. The stability of nanoparticles colloids was studied for one year and it is remaining stable for the whole investigation period. In this paper, the prepared gold nanoparticles colloids were stable for more than 12 months.



**Figure 3. SEM micrographs of different pretreated gold nanoparticles colloids (magnification  $\times 13000$ ) (a) Au21, (b) Au22 and (c) Au24.**



**Figure 4. AFM images for gold nanoparticles of Au24 sample and their particle size curve.**

In order to increase the stability life time of gold nanoparticles colloids prepared using Turkevich method, there was one of the reaction parameters that must be taken into consideration to be improved to give more dispersed gold nanoparticles with larger interparticle distance and consequently with higher stability. This parameter was the stirring power of the magnet stirrer used during the preparation condition. The same experimental procedure for gold nanoparticles colloids was prepared again taking into consideration this parameter, consequently deep red wine color of gold nanoparticles colloids, as shown in figure 5 was obtained. The prepared colloids had stability time more than one year.

Au21, Au22 and Au24 samples remain with the same color and identical UV-VIS spectra stay without any change for more than one year.

Figure 5 shows the photos of gold nanoparticles colloids with different experimental conditions according to table 1.



**Figure 5. Gold nanoparticles colloids prepared using Turkevich method with higher stirring power and stable life time for more than one year. From left to right Au21, Au22, Au24 and Au25.**

#### 4. Conclusion

Gold nanoparticles colloids were prepared using citrate reduced method (Turkevich method). The prepared colloid was subdivided into 4 parts to be treated as follows: as prepared, ultrasonically dispersed, centrifuged for 4000 rpm for 10 min and passed through nylon membrane. The different colloids were characterized using UV-VIS spectrophotometer for absorption studies, LV-SEM for microstructural and particle size distribution, AFM for particle size and interparticle distance interpretation. Good correlation between spectroscopic and SEM/AFM studies of the different colloids from the point of view of lower average particle size, higher degree of dispersion with moderate interparticle distance were obtained. This moderate interparticle distance was one of the important factors that determine the time of stability of the prepared gold nanoparticles colloids. The prepared colloids were stable for one year. In order to increase the stability of the obtained colloids, gold nanoparticles colloids were prepared using the same procedure but with a higher stirring power. Deep red wine color of gold nanoparticles colloid that is stable for more than one year was obtained with SPR band at 530 nm. So, not only the capping agent was the primary parameter that can determine the degree of dispersion of metal nanoparticles but there was another important factor: the power of magnet stirrer used during the preparation procedure that improved the degree of metal nanoparticles dispersion into the solution phase and the stability of the obtained metal nanoparticles colloids. So it was found that with a higher magnetic stirring power, a better stability of the prepared gold nanoparticles colloids for more than one year was achieved and so better applications performance could be obtained. The obtained gold nanoparticles were characterized by super opto-electronic properties that can be used in optical and opto-electronic devices, as well as many chemical applications.

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