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Formation Silver Nanoparticles of Different Size Using Different Reductants with $AgNO_3$ Solution

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Abstract
In this study, silver nanoparticles (AgNPs) are synthesized using different chemical routes to obtain different sizes and shapes of nanoparticles by colloid chemistry with using stabilizing and reducing agent, which make them interesting for variety of physical applications. The morphology and structure of the synthesized AgNPs were characterized by UV-VIS spectra, Scanning Electron Microscopy (SEM) and Zeta potential to demonstrate that different sizes and shapes can by synthesized by different reductants in the presence of various stabilizing agents.

Keywords: Silver Nanoparticle (AgNPs), stabilizing agent; Reducing agent, chemical method

تكوين جسيمات الفضة النانوية ذات الاحجام المختلفة باستخدام مختزلات مع محلول نترات الفضة

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الخلاصة:
في هذه الدراسة تم تحضير جسيمات الفضة النانوية باستخدام طرق كيميائية مختلفة للحصول على احجام واشكال مختلفة من الجسيمات النانوية باستخدام انواع مختلفة من المثبتات و المادة المختزلة والتي تجعل منها مادة مفيدة في كثير من التطبيقات الفيزيائية .وقد تم دراسة طبوغرافية وتركيب السطح لجسيمات الفضة النانوية المحضرة من خلال استخدام مطيافية الاشعة فوق البنفسجية والمجهر الالكتروني الماسح وجهد زيتا والتي اوضحت ان الاحجام و الاشكال المختلفة يمكن السيطرة عليها من خلال استخدام نوعيات مختلفة من المواد المثبتة و المواد المختزلة.

1. Introduction

In recent times, various attempts have been devoted to control the synthesis of various particles on nanometer and micrometer scale. Usually their size distribution and shape need to be well define for applications in physical, chemical, biological or even medical fields. In particular, metal particles, like silver colloids, are very attractive for potential applications, such as quantum dots or in miniaturization of electronic devices, because of their distinctive optical and electrical properties. These small particles are ideal catalysts and photo catalysts for many organic reactions due to their large surface area and extraordinary surface activity. Depending on synthesis methods and the kind of stabilizing and reducing agent, particles with various properties can be produce [1]. In addition, Ag nanorods have recently attracted large attention due to their interesting applications, which consist of photonic crystals [2], infrared polarizer's [3], and catalysts [4].

A range of chemical approaches have also been utilized to synthesis silver nanoparticles with different size distribution and different shapes [5-8]. Ag nanoparticles can be synthesized using various methods such as: chemical, electrochemical and Pulsed Laser deposition (PLD) ….etc. The

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most popular preparation of silver colloids is chemical reduction of silver salt ($AgNO_3$) by sodium citrate or sodium borohydride. This preparation is simple, but the great care must be applied to make stable colloid. Furthermore, it is important to control the growth of particle and the use of stabilizing agent to obtain nanoparticles. The stabilizing agent can be the reductant itself such as trisodium citrate or ethylene glycol. It can also be an additive and the polyvinylpyrrolidone (PVP) has been widely used [9].

Since, the chemical reduction methods are represented by the preparation of silver nanoparticles with controlling size in which silver ions are reduced by reductants and stabilizing or protecting agents to prevent agglomeration nanoparticles. The chemical method is often utilized to produce silver colloidal nanoparticles [10-11]. In this study, Silver nanoparticles (AgNPs) with controlled particle size were prepared using different reducing and protecting agents.

2. Experimental procedures

2.1 Preparation silver nanoparticles (AgNPs) using different reductant with and without stabilizing agent

Method 1: Silver nanoparticles (AgNPs) in aqueous solution were prepared by reduction of $AgNO_3$ with $NaBH_4$ and stabilized by using trisodium citrate. Briefly, 100 ml of a 0.12M aqueous $AgNO_3$ solution and 85 ml of 0.12M aqueous sodium citrate solution was prepared under magnetic stirring. Then, 0.6ml of a prepared 5mM aqueous $NaBH_4$ solution was added drop wise over 5min then stirring vigorously for 2h at 60 ^oC. After aging the solution for 2 h, a fixed volume of NaOH (drop wise) was added to 100 ml of solution which has a role to form nanorodes structure as shown in Figure-1 and keeps on stirred for 1h at 60 ^oC under magnetic stirring to observe the color change.

Method 2: In this method, silver nanoparticles were synthesized by using sodium borohydride ($NaBH_4$) and polyvinylpyrrolidone (PVP) as stabilizer by dissolving 0.074M of $NaBH_4$ in 10 ml cold distilled water, and then add 0.001M of PVP. Then $AgNO_3$ was prepared by dissolving 0.012M of $AgNO_3$ into the same solution (10 ml cold distilled water). Put the flask on magnetic stirrer for 1 h. at 65^oC at vigorous stirrer, and observed the cooler changes of prepared sample as shown in Figure-1.

Method 3: In other reaction, sodium citrate was used as the reducing agent. It was prepared by dissolving 0.00098M of $AgNO_3$ in 500ml distilled water, and then the solution was heated to boiling. Then 0.043M of trisodium citrate was dissolved in 100 ml distilled water and 5 ml of trisodium citrate were added to 500 ml of $AgNO_3$ after boiling (drop wice). During the process, the solution was mixed vigorously. The solution was left on hot plate for 1 hour at 80°C for heating only, then it was cooled to room temperature, the color was reddish green.

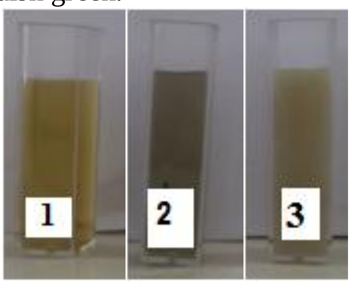

Figure 1-Photographs of different colors of obtained Ag nanoparticles prepared using different reducing and stabilizing agent method 1, 2, and 3, respectively.

2.2 Characterization of prepared AgNPs

Characterizations of the nanoparticles were achieved by different techniques. The absorption optical spectra of silver colloids were recorded using UV-Vis spectra (SP8001, Metertech). The morphology and structure of silver nanoparticles was measured with a scanning electron microscopy (SEM, the VEGA EasyProbe), and Zeta potential analyzer (Brookhaven Instruments Corporation).

3. Results and Discussion

3.1 UV-Vis spectra

UV-VIS spectroscopy is one of the most widely used techniques for structural characterization of silver nanoparticles. As shown in Figure-2 (a,b,c), absorption spectrum of formation Ag nanoparticles in different reaction media have Plasmon absorption band with a maximum peaks at 405nm, 410nm and 441.94 nm using method 1, 2,and 3, respectively indicating the presence of Ag nanoparticles and other irregular shapes like Ag cubic and Ag nanorods which have been synthesized by different types of polyol synthesis and also confirmed their nano size as shown by SEM photographs. Figure-2(a), indicating the presence of spherical Ag nanoparticles formed in the reaction media has maxima absorption at 405nm with an average particle size of 25 to 100 nm as deal with SEM analysis.

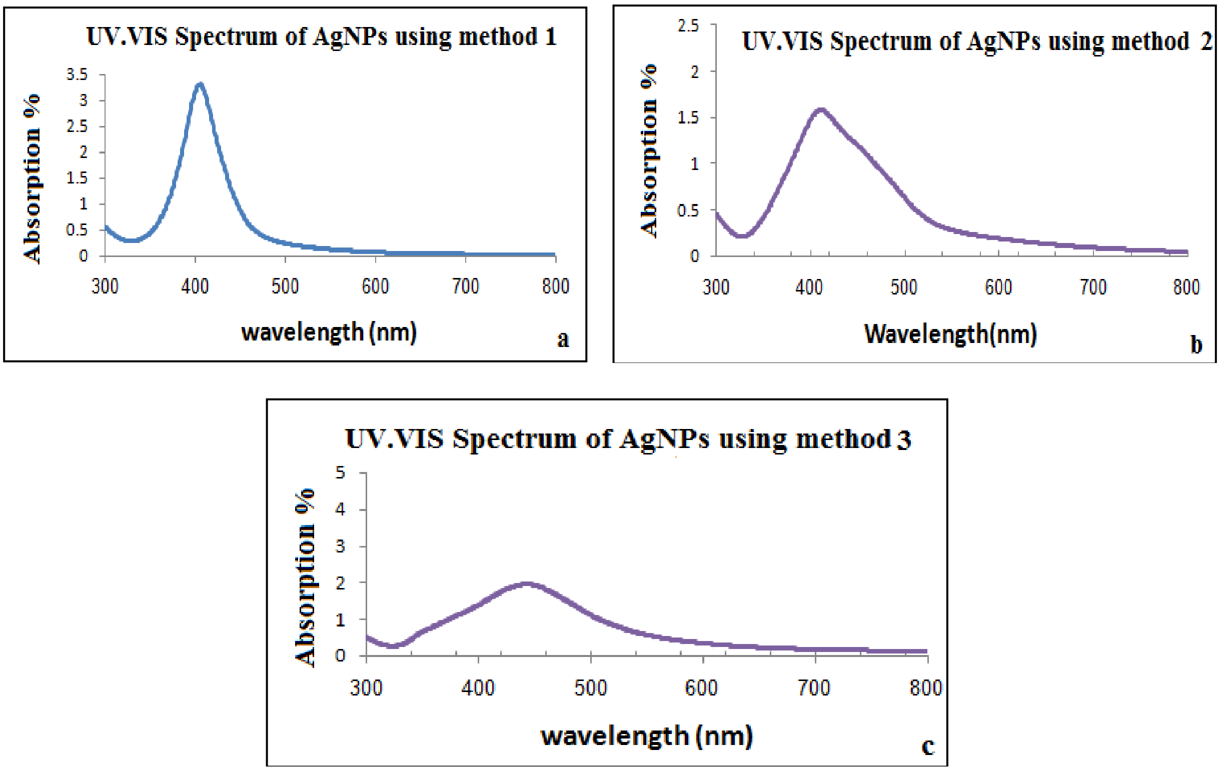

Figure 2-UV–Vis absorption spectra of silver nanoparticles obtained using different reductant with stabilizing agent a) method 1,b)method 2and c) method 3

In Figure-2(b), The adsorption spectrum of the dark yellow silver solution prepared by $NaBH_4$ reduction in the presence of PVP shows the Surface Plasmon Resonance (SPR) at about 410 nm, confirmed successful formation of AgNPs with different shapes and length like Ag nanowires, or Ag nanorods with average particle range from 25nm to 80nm and average length in the range from 1 µm to 2µm, respectively as compared with SEM analysis. While Figure-2(c) implies the formation of Ag irregular shapes like cubic with large average particle size greater than 100 nm with broaden absorption peak spectra shift towards larger wavelengths 441.94 nm using method 3.

3.2 SEM analysis

Figure-3(a,b) shows the SEM of the prepared sample using method 1 with spherical shapes which have a low surface area to volume ratio depending on the type of reducing agent which represented by $NaBH_4$ (strong reducing agent) and trisodium citrate with addition a drops of NaOH to control the shapes of AgNPs . Since, the average particle sizes in the range from 25nm to 100nm.

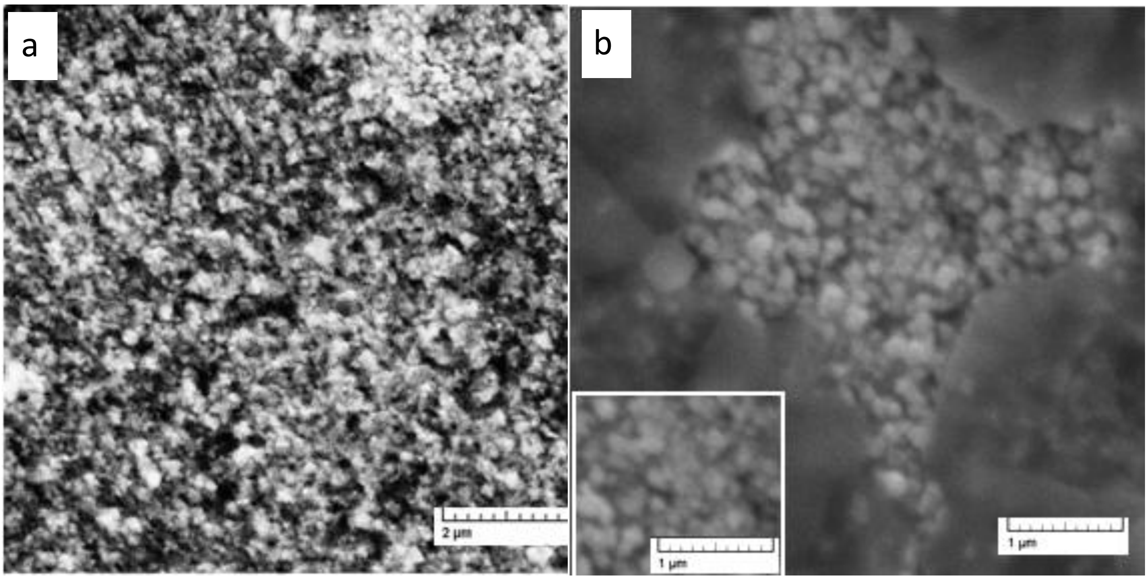

Figure 3- a,b) SEM micrographs indicates the formation of Ag nanoparticles using $NaBH_4$ and trisodium citrate in method 1

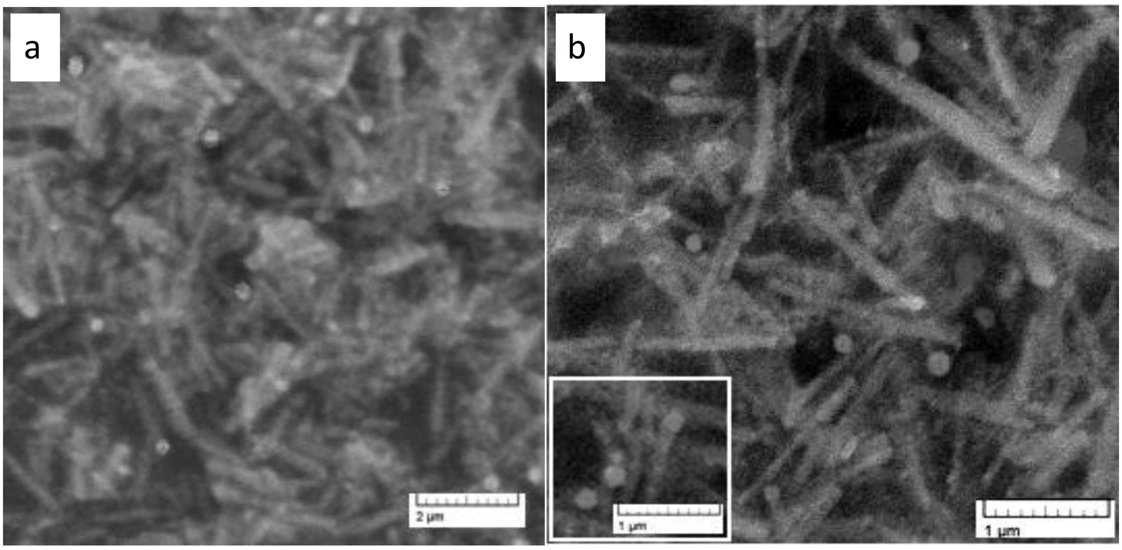

Figure 4- a,b) SEM micrograph of Ag nanoparticles and nanorods synthesized by method 2

For silver nanorods, the SEM images in Figure-4(a,b), illustrate the size and shape of the Ag particles resulting in heterogeneous structures that show the presence of spheres with average spherical cross section of rods 20 to 30 nm and rod-shaped with a average length about 1µm and average width 25 to 40 nm . These results indicate the growth process of the Ag nanorods with the assistance of PVP (stabilizing agent) and $NaBH_4$ (strong reducing agent). Since, PVP served to control the growth faces of crystalline faces, thus its concentration was critical to morphology. Besides, the addition of a stabilizing agent such as (PVP) to the reaction medium does not change the growth mechanism but affects the duration of each step and decreases the polydispersity. Despite the non-uniform shape of silver nanorods, we proceeded to evaluate the contrast properties of these nanorods. Homogeneous shape is not necessarily a prerequisite in all molecular imaging applications, provided the sizes of particles are within a desired range.

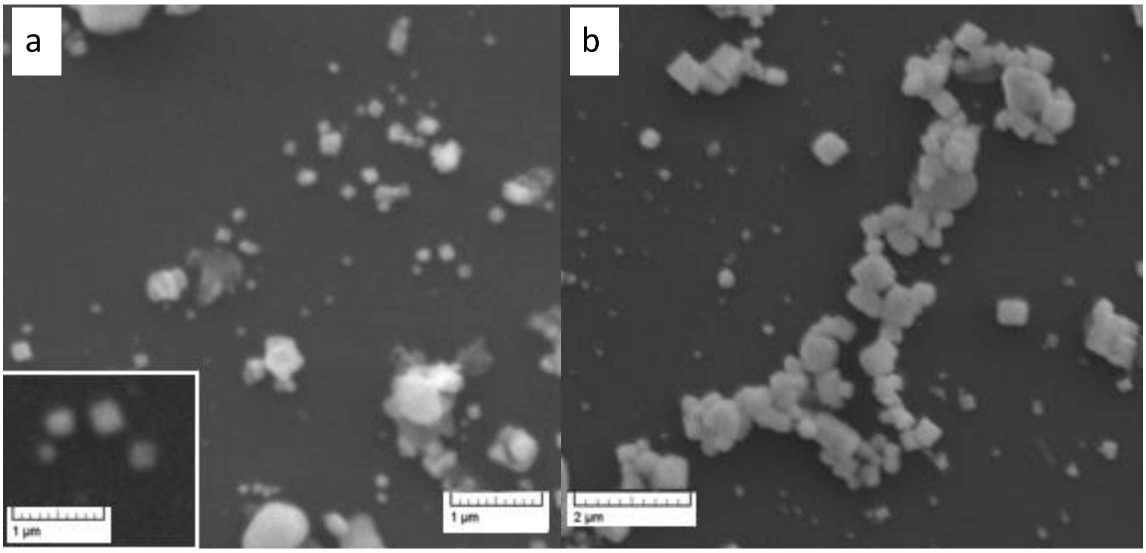

Figure 5- a,b) SEM micrograph of large Ag nanoparticles synthesized by method 3

Figure-5 (a,b) using SEM analysis at different magnifications indicates the formation of irregular shapes of Ag nanoprticles like cubic with large average particle size range from 40 and 200 nm using trisodium citrate alone without $NaBH_4$ as a strong reducing agent. Since, the results imply formation coarse grain sizes which have a low surface area to volume ratio when using a weaker reducing agent such as ascorbic acid produces larger particle sizes as compared with previous results.

3.3 Zeta potential analyzer

The Zeta potential is a key to determine the stability of colloidal dispersions and the magnitude of zeta indicate the degree of electrostatic between similar charged particles in dispersion. As shown in Figure-6(a,b,c), the formation of AgNPs using different chemical methods represented by a positive and negative value (**Zp=+37.29mV, -17.02 mV** and **-8.73 mV**) using method 1,2 and 3, respectively for characterization of stability in AgNPs suspensions. Since, the results indicate the stability of colloidal increased with decreasing the absolute value of zeta potential.

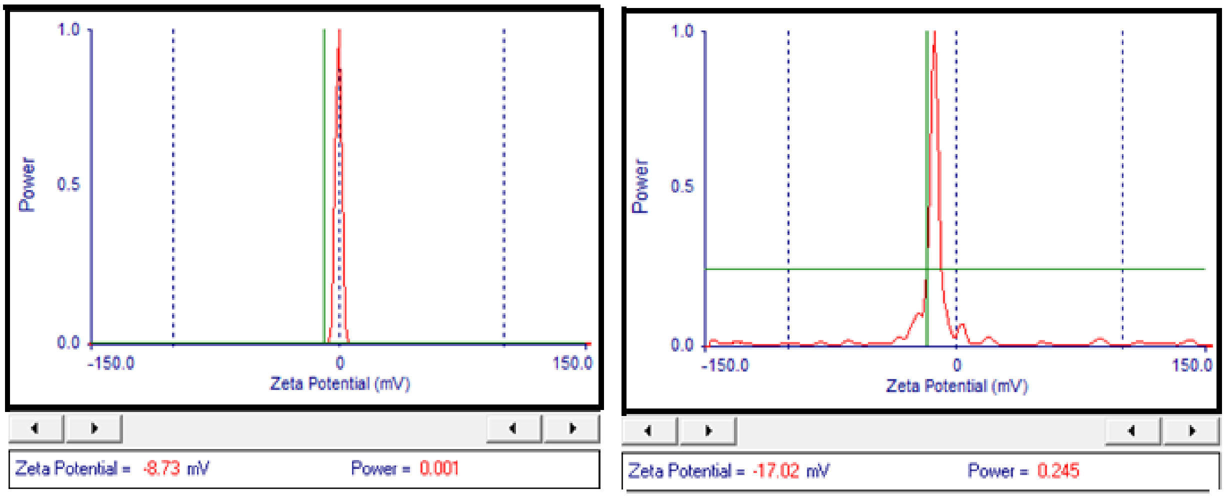

Figure 6- Zeta potential of stability in AgNPs suspensions using method a)1 ,b)2

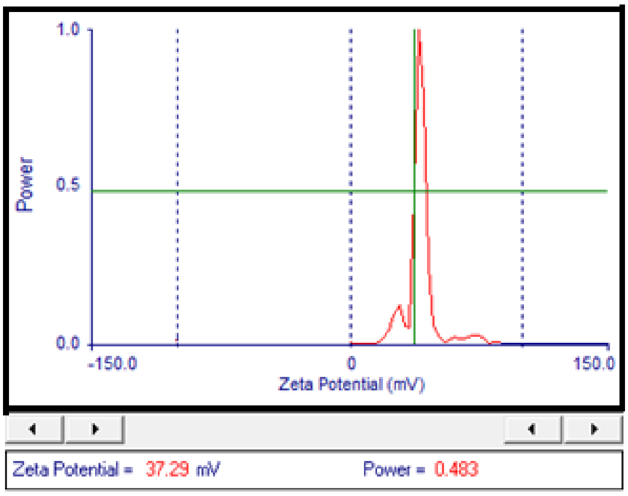

Figure 6- Zeta potential of stability in AgNPs suspensions using method a)1 ,b)2 and c)3

Conclusions

Our investigations of the synthesis of silver particles reveal the interaction between the strong reducing and weak reducing agent with or without stabilizing agent and metallic silver strongly affects the size and shape of the particles. Different morphologies and sizes of silver particles could be obtained in dependence of the additional reactants. Small and large Ag nanoparticles and different morphologies were characterized by UV-Vis spectroscopy and SEM techniques. From these measurements, it was evidenced that average particle size was between 25 and 100 nm using method 1 because of using strong reducing and weak reducing agents without stabilizing agent and formation a nanostructures of different morphologies like spherical shapes. In method 2, a nanorod structures with a average length about 1µm and average width 25 to 40 nm and spherical cross section of rods 20 to 30 nm due to the effect of stabilizing agent. While the addition of sodium citrate (weak reducing agent) to the boiling solution of $AgNO_3$ results in aggregating with large silver nanoparticles ad form irregular shapes like Ag cubic greater than 100nm . Since, these results showed that the limiting factor in the stability of silver nanoparticles the choice of the reducing agent. A change in the type of reducing agent such as sodium citrate, which is a weak reducing agent, resulted in aggregating silver nanoparticles as compared with method 1 and 2 that depend on addition of strong reducing and stabilizing agent.

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