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Synthesis and characterization of silver nanoparticles generated by cold plasma

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Abstract:

In this paper, silver nanoparticles (AgNPs) were synthesized using an atmospheric pressure non-thermal plasma method at different exposure time. XRD and Field emission scanning electron microscopy (FESEM) were used to investigate the structural and morphology properties of the silver nanoparticle. While optical properties were investigated using UV/VIS spectroscopy. The synthesized AgNPs appeared surface Plasmon resonance (SPR) centered at (398,402,400,390,395) nm. For all samples, the X-ray diffraction pattern revealed that the strong intensity peaks indicated crystalline nature and a face-centered cubic structure of silver nanoparticles. The AgNPs had an average crystallite size of 30.9 nm. Moreover, (FE-SEM) confirm the formation of Ag structure with particle sizes ranging (17−55) nm with spherical shapes. Results show that the plasma exposure time plays a crucial role in modifying the silver nanoparticles properties such as surface area, grain size, and optical stability.

Keywords: *Ag NPs, Non-thermal plasma , XRD , FESEM*

INTRODUCTION

One of the most active study fields in modern materials science is nanotechnology. It's a technique for getting great levels of precision in functions , shapes and sizes of materials and components by controlling the reaction of molecules and directing the atoms included in the reaction with specific direction allows for the most precise and refined products, as well as reduced energy consumption, than traditional production. Nanoparticles are particles with lengths ranging from 1 to 100 nm , two or three dimensions, according to the ASTM standard definition[1], Nanoparticles display new or fully optimized characteristics, such as molecule size, distribution, and morphology. The particles which have nano size are quite unique in nature due to the nano size increase surface area to the weight or volume ratio as well as their physical , biological and chemical properties is different to the relative of bulk material [2]. Among the diverse nanomaterials available, noble metallic nanoparticles have been used in a variety of application in the fields of electronic, magnetic, optoelectronics, and information storage [3] . Silver nanoparticles (Ag NPs) belong to the noble metal nanoparticles group. Due to their superior physical, chemical, and biological characteristics , silver nanoparticles (Ag NPs) have been

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extensively studied. Their superiority stems mostly from the shape, size, crystallinity, composition, and structure of Ag NPs as compared to their bulk forms. [4,5]. At present , nanoparticles of silver (Ag) and gold (Au) are utilized in a variety of biomedical, antibacterial, and anti-cancer treatments, drug transport, entomological, catalysis, , anti-biofilm , agriculture antioxidant, anti-fungal and parasitological applications. [6-12]

In this study focuses our attention to the synthesis using cold plasma (non-thermal) of silver nanoparticles is one of the newest fields in nanotechnology and nanoscience [13]. Cold Atmospheric pressure Plasma (CAP) is known as non-thermal because the electros have temperature much higher than other heavy particles, which are comparable to the room temperature [14]. Different methods have been used to prepare silver nanoparticles , such as laser ablation [15] , chemical synthesis [16] , micro-emulsions [17] , ionic liquids [18] , sol-gel method [19]. However, these methods may cause large silver nanoparticles or be not environmentally friendly , expensive and involve a special technique . Cold plasma treatment is a green technique and has recently attracted signiflcant attentions for efficient reduction of metal ions [20,21].

Experimental

Synthesize silver nanoparticles (AgNPs) by atmospheric pressure plasma jet. Aqueous solutions of Silver nitrate ($AgNO_3$) were prepared in concentration (1 mM) and different time (2, 4, 6, 8 ,10) min of plasma exposure. As a stabilizing agent , fructose was added to the solution at a concentration of 0.001 M and mixed with the ($AgNO_3$) solution. The experiment consists of a hole metal tubes of stainless steel with an inner diameter (1mm) and length (3cm) that connect to the cathode of high voltage direct current power supply. A small volume (10 ml) of prepared solution ($AgNO_3$) was put in a beaker. The beaker was placed upon the movement stage under the tube , , and the gap between the stainless tube's tip and the solution's surface was kept at 1 cm . A square piece of stainless steel foil (it's dimension 1cm x 1 cm) was immersed in the prepared solution and connected to the anode of the power supply. The stainless tube was connected to the Argon gas through flowmeter the flow of gas was adjusted to 2 (Litter per minute) and the discharge voltage was (6 KV). Figure (1) shows a photographic image of the experiment set up.

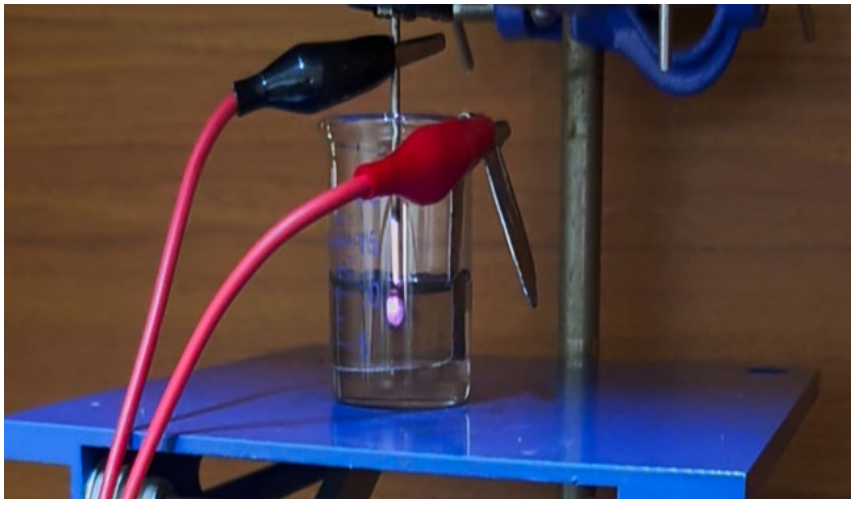

Fig 1. Show the cold plasma experimental setup in Liquid.

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Plasma of generated between the stainless tube and surface solution after switched on circuit . Initially, the color of the Silver nitrate ($AgNO_3$) solutions was transparent and it was varied to a dark brown after a few minutes of the treatment with plasma , which is the indicate the AgNPs formation . The AgNPs were not conglomerated and no deposition was observed, supported enough stabilization feature of fructose.

Results and Discussion

1- UV–visible (UV- Vis) absorbance

A cold plasma system was used to produce silver nanoparticles **.** The color change is an early indicator of the generation of Ag nanoparticles. The absorption spectrum of Ag nanoparticles is clarified in Figure (2) where the absorption peaks appear at (398,402,400,390,395) nm for $AgNO_3$ concentration (1 mM) at (2, 4, 6 ,8,10) minutes of plasma exposure , the color of the $AgNO_3$ solution changed from a transparent solution to a dark brown solution indicating the formation of Ag nanoparticles , because of the peak shifted to blue due to the surface plasmon resonance (SPR) of Ag nanoparticles where SPR occurs in specific metals such as silver and gold because of the arrival of its particle diameter to the nanoscale [22, 23] . The observed change in the absorbance peak intensity as a function of the plasma treatment time is demonstrated that plasma treatment technique was an effective way to synthesize the silver nanoparticles , the variation in absorption regions is due to the nano silver , while the variation of altitude peaks is due to the concentration of nano silver in solution . The absorption spectra result due to the interactions of free electron confined to silver nanoparticles with Plasma Exposure [24,25]

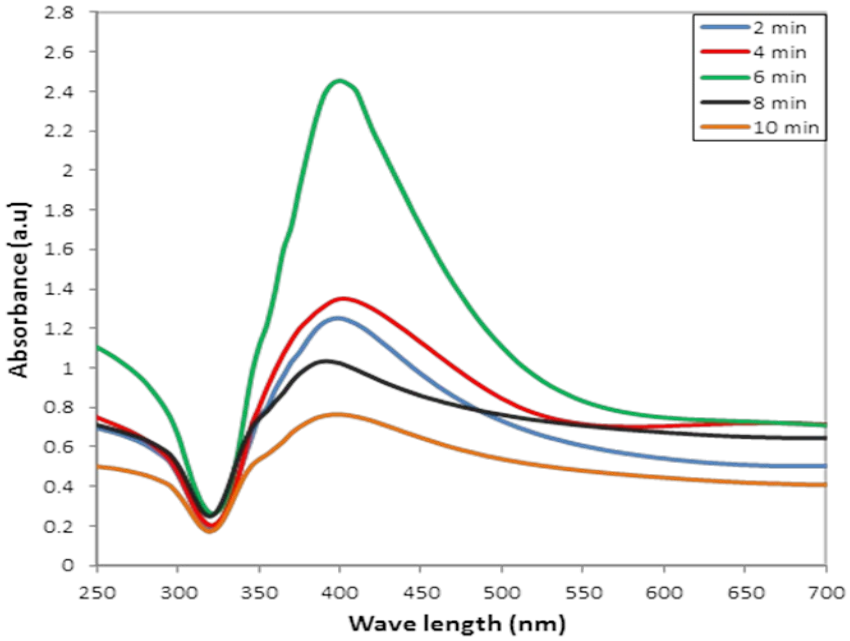

Fig 2. UV–VIS absorbance spectra of Ag NP_S at exposure times (2, 4, 6, 8, 10 min) with concentration (1mM).

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2- XRD analysis of Ag NPs

Figure (3) shows the X-ray diffraction pattern of prepared silver nanoparticles as afunction of exposure time (2, 4, 6, 8, 10 min) at concentration (1 mM) of silver nitrate ($AgNO_3$), the peaks detected at (2Θ= 38.1°) and (2Θ = 44.27°) assigned to the formation of cubic silver nanoparticles (JCPDS reference code : 04-0783) , the results of XRD pattern showed adiffraction pattern from silver nanoparticles with a fcc crystalline structure , other peaks observed at (2Θ = 46.14 °, 47.7 °, 54.75 °, 55.55 °, 56.47 °) attributed to the orthorhombic silver nitrate (JCPDS reference code: 84-0713). It was observed that increasing the plasma exposure time (2, 4, 6 min) led to high-intensity peaks which demonstrate that the phase development depends on the exposure time to improve the crystalline growth . The peaks became more clear and defined at time (6 min) , the increase of the exposure time (2 , 4 , 6 min) leads to rising (completion) of the crystallization process , the silver nitrate ($AgNO_3$) peaks are more clear and defined at time (8,10 min) while the silver nanoparticles peaks decrease [26,27]

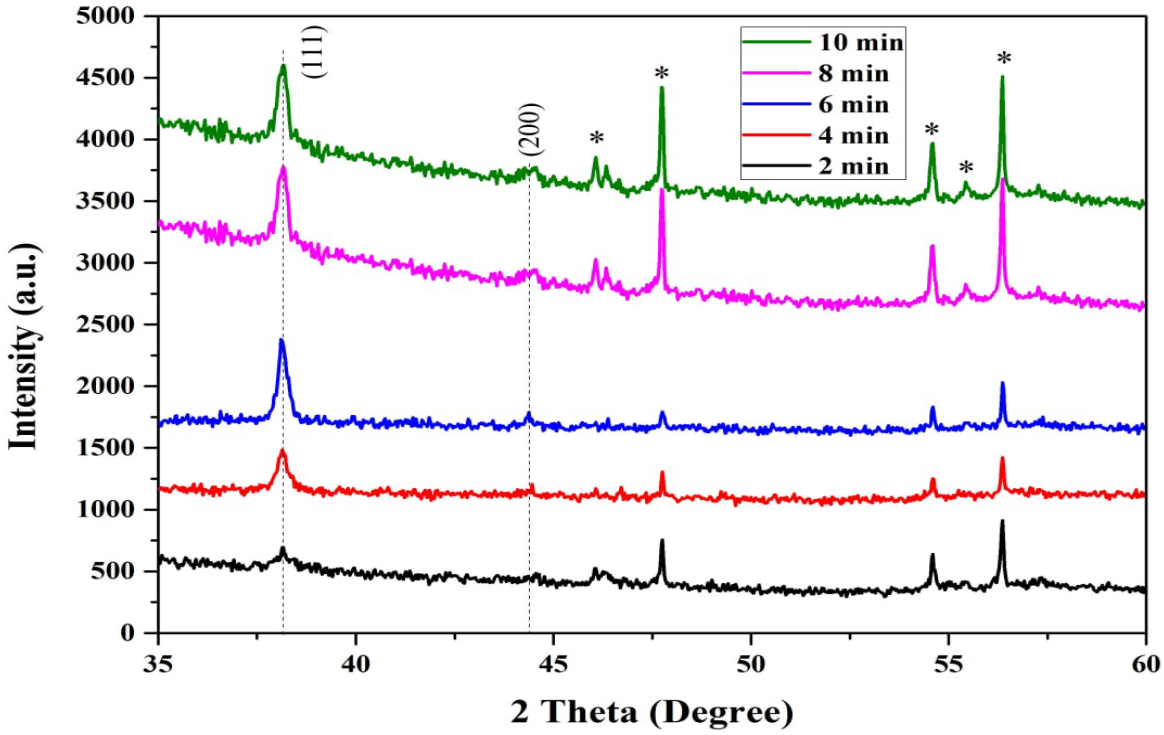

Fig 3. XRD pattern of Ag nanoparticles at different times (2, 4, 6, 8,10 min) with concentration (1 mM).

The average crystalline size of prepared silver nanoparticles at different times was calculated to be (30.9 nm). Table (1) shows the XRD calculations of silver nanoparticles at different times with concentration (1 mM).

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Table 1. XRD calculations of Ag nanoparticles at different times

2Θ (deg) Practical	2Θ (deg) Standard	FWHM (deg)	Crystalline size (nm)	d_{hkl} (°A) Practical	d_{hkl} (°A) Standard	(hkl)
38.115	38.117	0.31147	23.87	2.359	2.359	(111)
44.366	44.279	0.19385	37.94	2.040	2.044	(200)

The crystallite size (D) of AgNPs was calculated using Scherer equation below [28]:
$D = 0.9\lambda / \beta \cos\theta$ ……. (1)
λ : wavelength (1.5406A°) , β: full width half maximum , θ : angle of the peak

3 - FESEM Measurement of silver nanoparticles

The morphologies character of prepared silver nanoparticles were evaluated by FESEM measurement , Figure (4.5) shows the microscopic images of Ag nanoparticles of different exposure time (2, 4, 6, 8, 10 min) of plasma at (1 mM) of $AgNO_3$ concentration, the obtained images reveals that the particle size of prepared silver nanoparticles is variable and is within the range of (17−55) nm. The average particle sizes are (33.21, 45.13, 47.16, 36.25, 26.05 nm) at the plasma exposure time (2, 4, 6, 8, 10 min) respectively.

The Ag were crystalline , face centered cubic and almost spherical nanoparticles . The particle size of Ag nanoparticles gradually increases with the plasma reaction time of (2, 4, 6 min) , while the particle size decreases at the plasma reaction time (8 and 10 min). Observed that when the size of the metal nanoparticle becomes larger with the plasma reaction time (2, 4, 6 min); the radiation effects on the size became more important , where the electronic cloud displacement will become no longer homogenous for spherical nanoparticles, which leads to induced high multi-polar charge distributions [14, 15]. While at (8, 10 min), the particle size decreased , which is attributed to the plasma effect that led to the reconstitution of $AgNO_3$ salt as shown in the UV-vis test.

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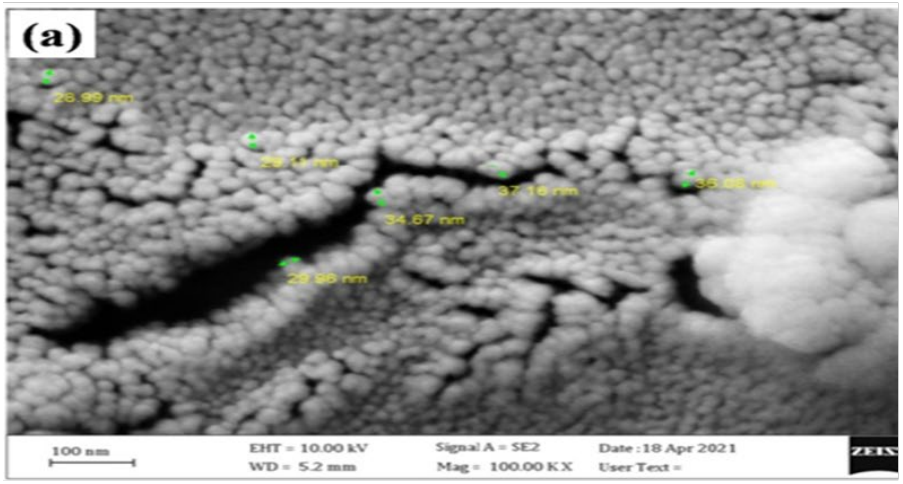

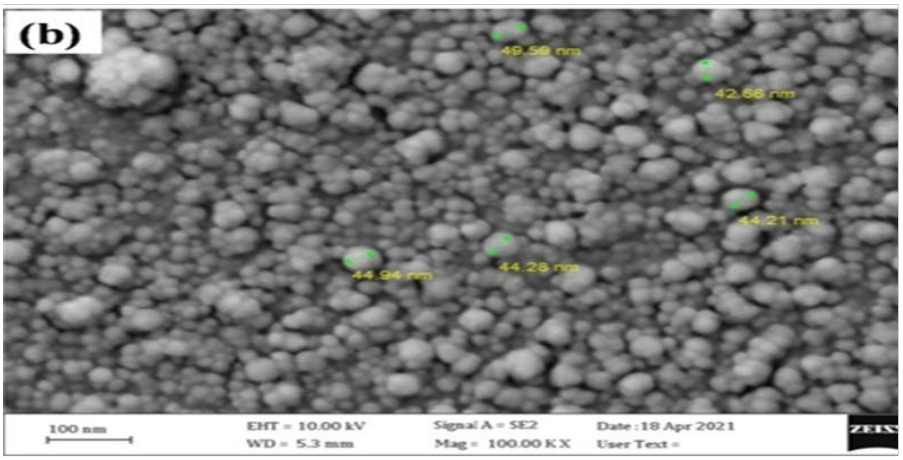

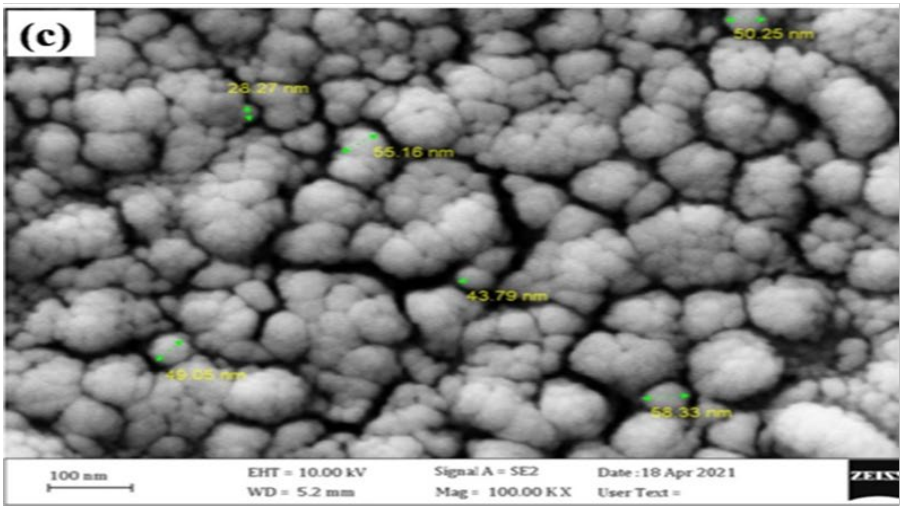

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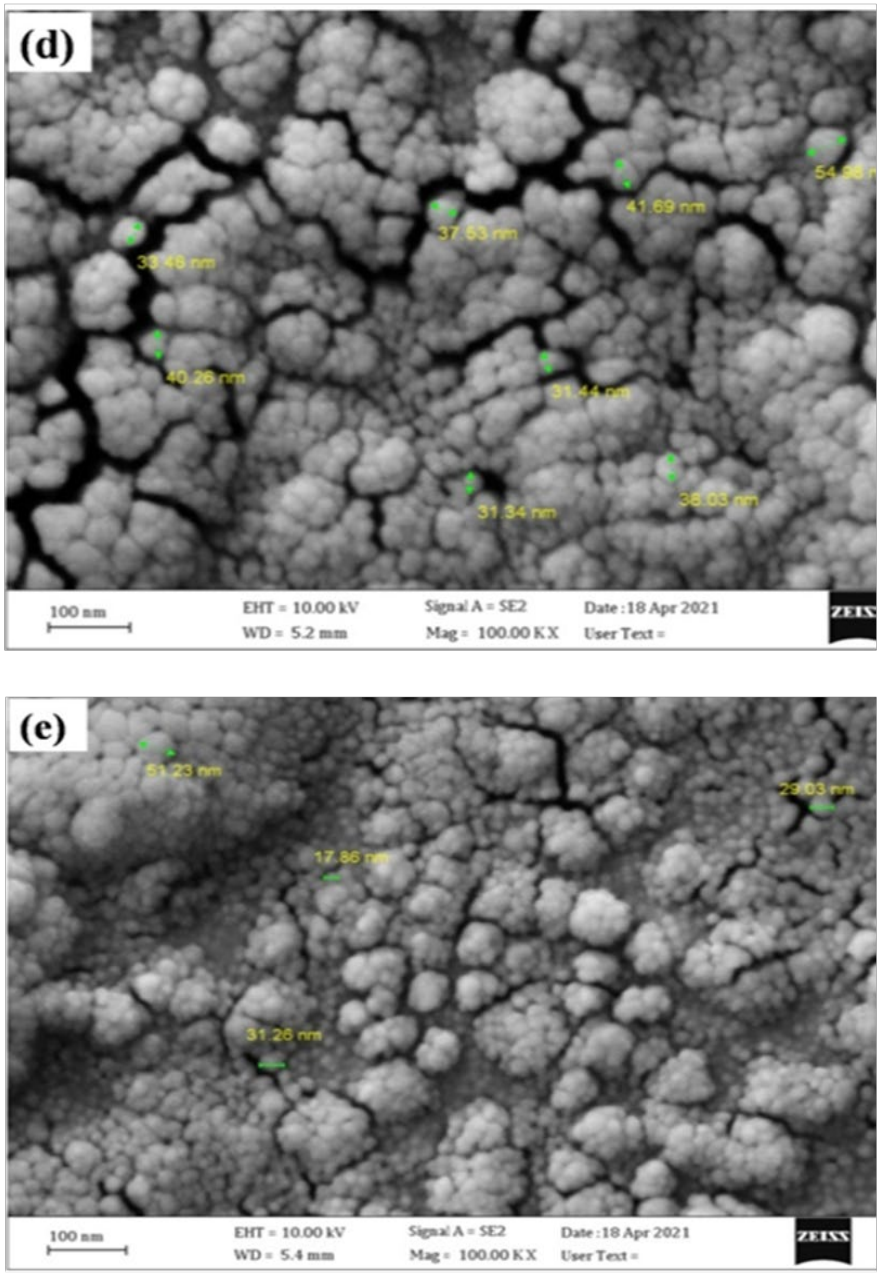

Fig 4. The microscopic images of Ag nanoparticles of exposure times
(a) 2min , (b) 4min , (c) 6min , (d) 8min , (e) 10min at (1 mM) of AgNO3

Conclusions

In the current work, silver nanaparticles are manufactured using non-thermal atmospheric plasma in an easy and fast way. The absorption spectrum peaks which analyzed by UV/VIS spectroscopy was (398,402,400,390,395) for Ag NPs. The presence of silver nanoparticles was confirmed by x-ray diffraction Pattern. It is found that the strong peak of silver nanoparticles is about 38.1°. From

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the experiment, it was found that the effect of the exposure time of plasma on average particle size where the average particle size of Ag nanoparticles gradually increases with the plasma reaction time of (2, 4, 6 min) , while the average particle size decreases at the exposure time (8 and 10 min) according to FESEM measurement

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