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Investigation the parameters affecting on the synthesis of silver nanoparticles by chemical reduction method and printing a conductive pattern

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Abstract

One of the widely used methods for the synthesis of silver nanoparticles (Ag NPs) with good dispersion is chemical reduction method in the presence of polyvinylpyrrolidone (PVP). In this paper, we describe the synthesis Ag NPs using silver nitrate as a source of silver ions, PVP as a protective agent and glucose as reducing agent. In order to achieve the smallest average particle size, the influence of the mass ratio of PVP/$AgNO_3$, glucose/$AgNO_3$ and reaction temperature to the size distribution of Ag NPs was investigated. The smallest particle size (40nm) can be obtained by temperature 60°C, weight ratio of glucose to silver nitrate 2.5g/g and weight ratio of PVP to silver nitrate 1.6g/g. Synthesized AgNPs are characterized by scanning electron microscopy, X-ray diffraction, and UV-Vis spectroscopy. Results showed that the particle size of silver nanoparticles less than 100 nm with a narrow size distribution and high purity is prepared. These particles were used to prepare a conductive pattern applied on a glass plate and the patterns with resistivity as low as 3.1μΩcm can be obtained. The results revealed that PVP polymer plays an essential role in obtaining nanoparticles with a good specification.

1. Introduction

In recent years, Nanoparticles of noble metals are of great interest because of their potential applications in different branches of science. Because of their small size (<100nm), nanoparticles exhibit a unique physical, chemical, biological and environmental properties, which have increased their applications in research, industry, agriculture, environment and medicine [1,2]. Of all the types of nanoparticles, Silver nanoparticles (Ag NPs) have attracted a lot of attention in the electronic industry due to the undisputed advantages in terms of chemical, physical and electrical properties and also providing interesting plasmonic and antibacterial properties [3]. When the size of these metal nanoparticles is small (<100 nm), these plasmon absorbance occur in the visible region of the electromagnetic spectrum, giving rise to colored solutions. One of the unique characteristics of plasmon excitation is the conversion of light energy into extreme and highly localized heating at the surface of these particles. In addition, silver Nano colloid itself has superior thermal conductivity and electrical conductivity that is widely known to industrial areas. Using silver Nano colloid, it is possible to produce conductive inks that not only using existing printing circuit plate, but also PET film to print circuit by the ink jet printer [4]. Currently, printed electronics technology has noticeable benefits such as a simple process, low-cost, reduction of waste and capability of various substrates, compared with conventional processes saving a lot of time and avoiding unnecessary processes. In addition to, silver nanoparticles have been used in solar cells to enhance absorption of sunlight and improve efficiency of solar cells, which is considered a special application of silver nanoparticles [5]. The main problem in preparing stable and printable inks containing Ag NPs for inkjet printing is to overcome the strong agglomeration of the particles in a dispersion medium besides to obtaining small particle size and narrow size distribution. For these reasons the synthesis and preparation of metal nanoparticles are highly regarded. However, there are several methods for creating nanoparticles, including physical and chemical methods which have been reported in the literature [6]. Among the numerous and diverse methods for the synthesis of silver nanoparticles is a chemical method because of its convenient operation, ease of control and simplicity. The reduction of silver ions to silver metals can be achieved by correct choosing of the type and quantity of reducing agent which plays an essential effect on the size and morphology of the silver nanoparticles. The amount of reducing agent required in a typical reaction is normally decided by the quantity of metal salt at the starting point while the type of reducing agent depends on what is the function of reducing agent in the preparation of nanoparticles. Another parameter which effects on silver nanoparticles synthesis is the capping agents. As the reducing agent transforms the metal ions into elemental metal, which then grows into a particle and the capping agent is responsible for preventing the uncontrollable growth of particles, prevent particle aggregation, controls growth rate, controls particle size and allows particle solubility in various solvents. These possibilities can be achieved by electrostatic stabilization or steric stabilization [7].

In the formation of silver nanoparticles by the chemical reduction method, the particle size and aggregation state of silver nanoparticles are affected by various parameters, such as initial $AgNO_3$ concentrations, reducing agent/$AgNO_3$ molar ratios, and stabilizer concentrations. Besides that, this method also can control the morphologies with the strongly during the synthesis because it depends very strongly on the temperature adopted. Based on this method also, the size of particles will achieve in the range 10 to 100 mm.

The main scope of this study is to produce silver nanoparticles by the chemical reduction method using glucose as reducing agent and polyvinylpyrrolidone (PVP) as a stabilizing agent. The effects of several processing variables such as glucose/$AgNO_3$, PVP/ $AgNO_3$ weight ratios and temperature of reaction were investigated. Finally, a conductive pattern was printed on a glass with synthesized powder and its electrical resistance was measured using a four-point probe.

2. Experimental details

2.1. *Materials*

All chemicals used in the experiment were analytic grade (AR) and used without further purification. The silver nitrate (99%) was provided by Rectapur Prolabo Co., Glucose and ethylene glycol (EG) were purchased from Merck, Polyvinyl pyrrolidone (PVP) (MW=10000) was obtained from Sigma-Aldrich, Ethanol (99%), sodium hydroxide (98%) and acetone were obtained from Merck, and distilled water.

2.2. *Synthesis of AgNPs.*

In the formation of silver nanoparticles by the chemical reduction method, the particle size and aggregation state of silver nanoparticles are affected by various parameters, such as initial $AgNO_3$ concentrations, reducing agent/$AgNO_3$ weight ratios, and stabilizer concentrations in addition to temperature [8]. In this research, three parameters, namely glucose/$AgNO_3$, PVP/$AgNO_3$ weight ratios and reaction temperature will be controlled to find a reliable way for manufacturing Ag NPs with certain characteristics as depicted in **table 1** and **table 2**.

Table 1. Shows selected parameters and its values.

Parameters	PVP/$AgNO_3$ (Weightratio)	Reaction temperatures (ºC)	Glucose/$AgNO_3$ (Weightratio)
Code	A	B	C
Series 1	1	30	2
Series 2	1.6	60	2.5

Table 2. Conditions for synthesis silver nanoparticles.

Test No.	PVP/$AgNO_3$	Reaction Temperature (ºC)	Glucose /$AgNO_3$
1	1	30	2
2	1	30	2.5
3	1.6	60	2
4	1	60	2
5	1.6	60	2.5

Silver nitrate solution (A) was prepared by adding a 0.36g of $AgNO_3$ into 30 ml distilled water and silver nitrate solution was obtained. The PVP solution (B) was prepared by dissolving 0.24g of PVP in 40 ml distilled water and heated to 60ºC with rigorous mixing. The glucose and sodium hydroxide solution (C) were prepared by dissolving 0.36g of glucose in 40 ml distilled water. Then the solution (B) was added to the solution (A) giving a yellow solution which was added in C drop by drop at determining temperature with stirring for 10 min more. The obtained particles were separated by centrifugation, and the solid products were washed with distilled water and ethanol several times until no NO_3^- could be traced. Then the product is placed at room temperature for 24h to become dry. The obtained Ag NPs are characterized by X-ray diffraction and UV-Vis spectroscopy. The size distribution of synthesized Ag NPs powder was investigated by scanning electron microscopy (SEM) technique.

2.3. *Preparation of conductive pattern.*

The Ag NP-based conductive inks were prepared by directly vigorous dispersing in a mixture of ethylene glycol: ethanol: water at a weight ratio of 7:2:1 for approximately 10 min, the weight percentage of Ag NP-based conductive inks is ca. 35 %, The percentages are by weight based on the weight of the conductive ink. Finally, the silver nanoparticles inks were printed onto clean glass surface with dimensions 1x5cm. The patterns were sintered at 270°C for 30 min in argon oven.

It is essential to cure the layer in order to remove excess solvent and increase the conductivity of the silver ink. A curing process also provides the benefit of increasing the adhesion of silver ink tracks on the substrates. After the completion curing step, electrical resistivity was evaluated. It is important here to point out that the basic requirements for metal-based inks are similar to those of standard inkjet inks, but in addition, they should provide a good electrical conductivity of the printed patterns. In addition, the dispersion of the nanoparticles in ink should be good in order to avoid any aggregation [9].

2.4.*Characterization of AgNPs and ink.*

Characterizations of the particles and ink were achieved by different techniques.

2.4.1. *UV-visible measurements.*

Spectral analysis for the development of nanoparticles at different reaction conditions were observed using JASCO V-730 - UV–Vis spectrophotometer from 190 to 1100 nm at a resolution of more than 1.5at room temperature.

2.4.2. *SEM analysis.*

Scanning electron microscope (SEM) model VEGA II XMU from TESCAN company the USA was used to determine the shape of developing nanoparticles. Samples were prepared by depositing a drop of colloidal solution on an aluminum grid sample holder and drying at room temperature.

2.4.3.*XRD analysis.*

X-ray diffraction (XRD) was used to determine the crystal structure of particles. X-ray diffraction (XRD) measurement was performed on X-ray diffractometer (Philips Xpert Powder XRD) with Cu Kα radiation (λ = 1.5418 A°), operated at 30 kV and 100 mA and spectrum was recorded by CuKα radiation with wavelength of 1.5406 Å in the 2θ range of 20°–90°. Samples were prepared as uniform thin films supported on the slides.

2.4.4. *Electrical resistivity*.

The printed patterns resistances were determined using a four-point probe (SES Instruments Pvt. Ltd, India).

3. Results and Discussion.

3.1. *XRD analysis of synthesized Ag NPs and reaction mechanism.*

In order to study the phase formation in samples synthesized by the chemical reduction method, X-ray diffraction was used. The structure of the synthesized Ag NPs is characterized by XRD as depicted in Figure 1. Clear five diffraction peaks at 2θ of 38.18°, 44.32°, 64.50°,77.05° and 81.89° respectively could be indexed as (111), (200), (220), (311) and (222) Bragg's reflections of the face-centered cubic (FCC) structure of silver. Furthermore, there is no other diffraction peaks relating with Ag_2O are found, indicating that the prepared sample is highly purified Ag NPs(more than 99%).

During the experiments, color changes in the solutions were noticeable. Firstly, the solution color was light yellow after adding silver salt solution to PVP solution. However, after a short amount of time, the color change was seen and the solution turned dark yellow, indicating the slow formation of nanoparticles and PVP, in this case, has a dual role here; it functions as a stabilizing agent as well as a reducing agent through its end aldehyde group.Certainly, Polyvinylpyrrolidone is a very weak reducing agent and do not have the ability to reduce all silver ions. So, in the second stage, the possible reaction between glucose and the silver ions in the presence of polyvinylpyrrolidone and sodium hydroxide as reaction accelerator can be written as [10-12]:

$$Ag^{+} + PVP \rightarrow Ag\left(PVP\right)^{+} \quad (1)$$

$$CH_2OH-(CHOH)_4-CHO+2\left[Ag\left(PVP\right)\right]^{+}+2OH^{-}\rightarrow CH_2OH-(CHOH)_4-COOH+2Ag(PVP)\downarrow+\mathrm{H}_2O \quad (2)$$

$$2Ag^{+}+2OH^{-}\rightarrow Ag_2O+H_2O \quad (3)$$

$$Ag_2O+CH_2OH-(CHOH)_4-CHO+2PVP\rightarrow CH_2OH-(CHOH)_4-COOH+2Ag(PVP)\downarrow \quad (4)$$

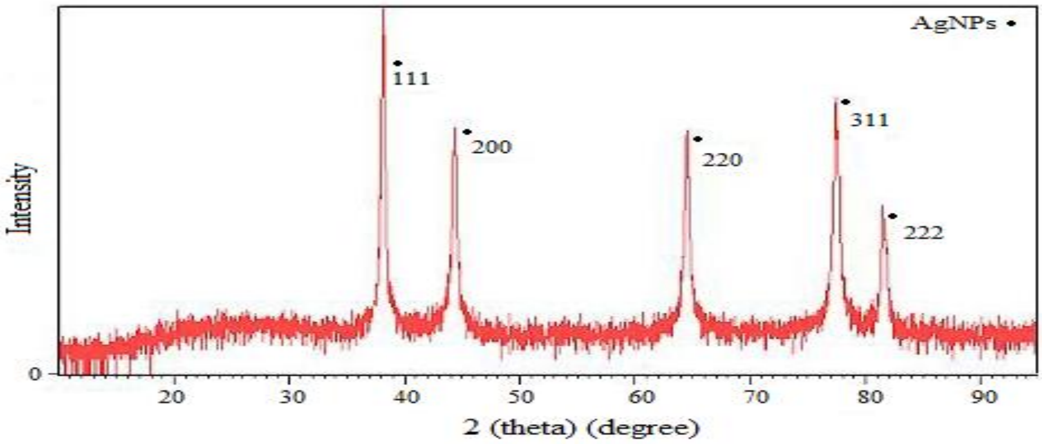

Figure 1. The XRD spectrum of Silver particles.

In an $AgNO_3$ solution containing PVP, silver ions were reduced in two–step process. The first was silver ions (Ag^+) compounded with PVP and complex ions were produced (Eq.1). The hydroxyl ion may undergo a nucleophilic addition reaction to glucose producing gluconate ions and then it reduces silver ion to the silver atom (Eq.2). The other two equations (3 and 4) were the second process of the reaction. In equation (3), Ag^+ reacted with the hydroxyl ion producing Ag_2O and then the product, Ag_2O, was reduced by glucose and silver particles were generated (Eq.4). According to Chou et al, it is possible that at the beginning of silver ion reduction some Ag_2O is formed, which later serves as nuclei for the subsequent formation of Ag colloids [10].

In the process of reaction, the stabilizing agent formed a protection layer on the surface of silver oxide and silver particles [12].A primary purpose of the introducing PVP was to protect the silver nanoparticles from growing and agglomerating because the donate lone pairs of both oxygen and nitrogen atoms on the polar groups of one PVP unit may occupy two sp orbitals of silver ions form a complex compound which easily promotes the nucleation of metal ions and PVP prevents Ag nanoparticles from agglomerating through the steric effect [7]. In the literature, PVP molecular weight has a great effect on forming nanoparticle size, which shows that larger PVP molecular weight has a long polymer chain, which means that the repeating units is more in the polymer chain and can accommodate a number of silver atoms [13].Shin et al. Reported how the growth of the Ag nanoparticles is affected by variation in the molecular weight of PVP [14]. Also, Chou et al. Investigated the effect of PVP molecular weights on the formation Ag nanoparticles. They found that the size of Ag nanoparticles could be controlled by using different molecular weights of PVP [10]. In addition, the chemical bond between PVP and particle surface of silver is so strong that up to 6 times washing with water and acetone again particle surface is not completely clean and this chemical bond is strong enough to prohibit aggregation of silver particles. When the polymer/silver nitrate ratio more than 1.5 the particle surface is completely covered with the polymer [15].

3.2.*UV-visible measurements.*

UV-Vis spectroscopy is shown in Figure 2. It is observed that a characteristic absorption peak at approximately 410 nm indicates the presence of silver nanoparticles [16].

3.3. *SEM analysis and electricalresistivity.*

Scanning electron microscopy (SEM) was used to determine the morphology (size and shape) of nanoparticles. The SEM images of the prepared Ag NPs show that they have a spherical shape and well-dispersed(Figures 3, 4, 5 and 6). Ag nanoparticles range in size from 40 to 122nm as demonstrated in **table 3.**It is clear from table 3 that the smallest sample size is 5 and the largest size is sample 1. It is possible that a larger amount of silver nanoparticles with small particle size can be achieved.

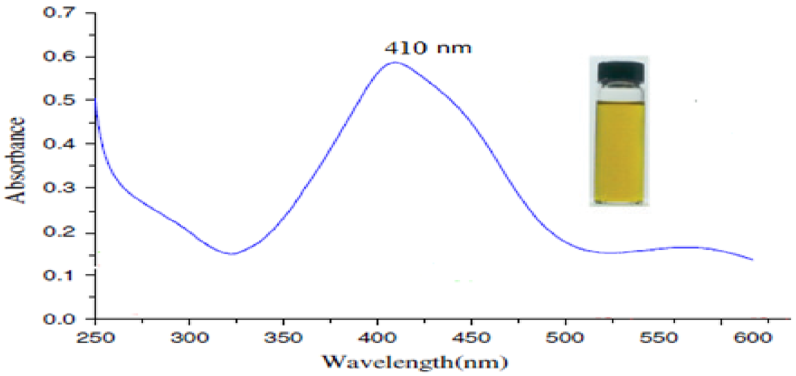

Figure 2. UV-Vis. Absorption spectrum of an aqueous solution of spherical Ag NPs as well as an image of this colloidal solution (inset).

Table 3. Average size of nanoparticles and electrical resistivity.

Test No.	Average size of nanoparticles (nm)±6	Electrical resistivity (μΩ.cm)
1	122	8.9
2	85	4.8
3	59	3.9
4	65	4.1
5	40	3.1

The electrical resistivity of silver nanoparticles thermally cured is an important parameter that must be characterized after printing and sintering process which express the actual performance of the conductor. Therefore, the electrical resistivity of printed patterns measured by using the four-point probe and the results are listed in **table 3**. Additionally, the resistivity of printed patterns is significantly influenced by the sintering time and the critical curing temperature. The critical curing temperature is defined in this case as the temperature at which the printed sample becomes conductive, *i.e.* having a resistance lower than 40MΩ [17]. Notably, if the sintering temperature exceeds a critical value, grain growth of nanoparticles can occur and therefore increases the electrical resistivity of the pattern. Whatever, in some cases, thermal sintering at temperatures away from the critical temperature, the electrical resistivity of printed patterns becomes equivalent to that of bulk silver [3]. In this study, sintering temperatures were fixed for all 5 tests. In experiment 1 because of the incomplete sintering process, larger particles are obtained, then the electrical resistivity is increasedbecause ofthe incomplete sintering process.

3.4. *Effect of reducing agent concentration on the silver particle size and the size distribution.*

The first series of experiments were performed by changing the concentration of the reducing agent. This led to different ratios of reducing agent to silver salt in the reaction mixture. The reaction mixture concentration of the silver salt was kept constant throughout all experiments. Experiments 1 and 2 were performed at a constant temperature. As seen in table 3, by increasing the concentration of reducing agent the size of particles decreases. In test 1, the concentration of reducing was lower than in test 2 so we can say that the concentration of Ag^+ in test 1 is greater than in test 2. Consequently, we could conclude that the concentration of Ag^+ has a great effect on the growth rate of AgNPs then the average size of particles in test 1 is greater than in test 2. Figure 3 shows the scanning electron microscope image of silver nanoparticles obtained from test 1 and test 2.

3.5.*Effect of stabilizing agent concentration on the silver particle size and the size distribution.*

The second series of experiments were performed by changing the concentration of the stabilizing agent. This led to different ratios of PVP to silver salt in the reaction mixture. The reaction mixture concentration of the silver salt was kept constant throughout all experiments. Experiments 3 and 4 were performed at a constant temperature. As seen in table 3, by increasing the concentration of PVP, polymer chains coated completely the surface of the particles and protect them from the aggregation to form larger particles. It exhibits favorable protecting properties due to its unique structure as demonstrated above. As a result, particles are fine and have a more uniform morphology as depicted in figure 4.

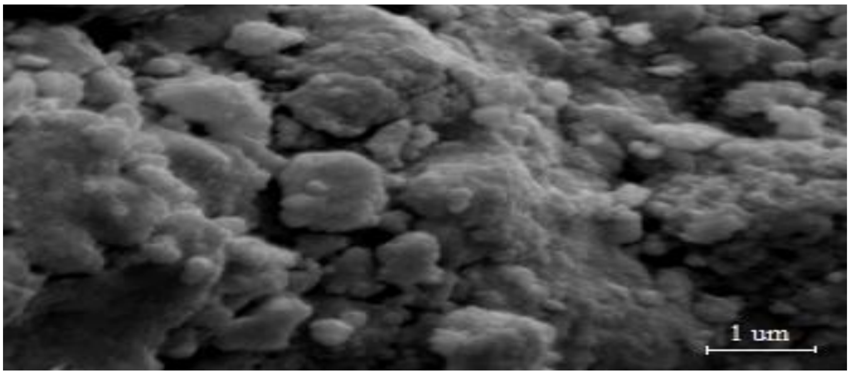

Figure 3. SEM micrograph of Ag NPs produced from test 1 and test 2.

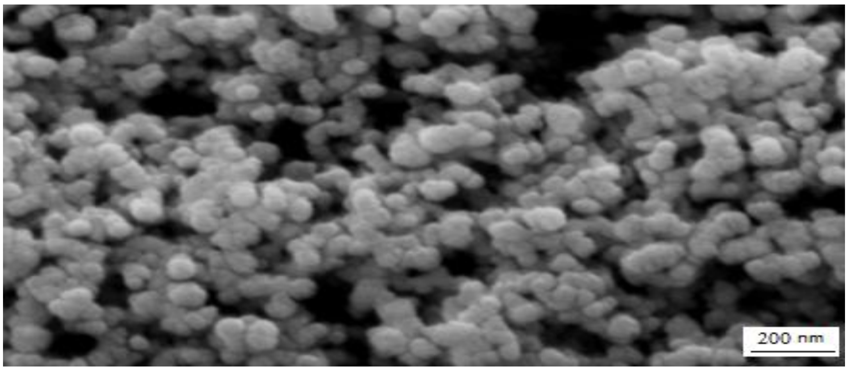

Figure 4. SEM micrograph of Ag NPs produced from test 3.

3.6.*Effect of temperature on the silver particle size and the size distribution.*

The third series of experiments entailed onlythe variation of reaction temperature while keeping other parameters unchanged. As a result of test 1 and 4, we found that the 30°C temperature has an immense effect on particle size as depicted in table 3. This is because glucose at thistemperature has a limited reducing power and with increasing the temperature reducing efficiency increased. Figure 5 shows the scanning electron microscope image of Ag NPs obtained according to test 1 and 4 conditions.

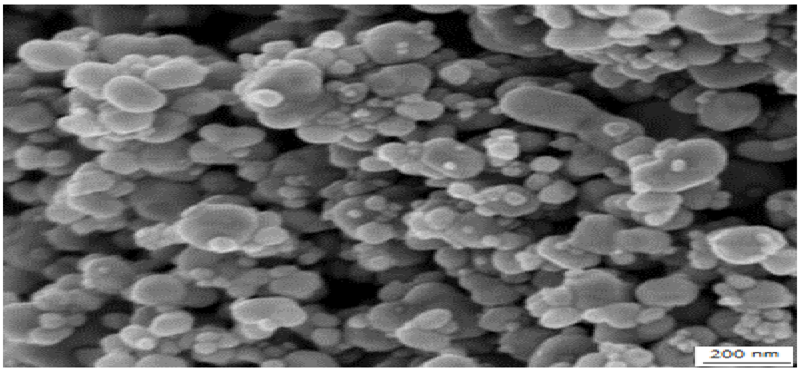

Figure 5. SEM micrograph of Ag NPs produced from test 1 and test 4.

In contrast, the well-dispersed quasi-spherical-shaped silver particles and a good narrow particle size distribution (Figure 6) were obtained in the case of PVP/$AgNO_3$=1.6, Glucose/$AgNO_3$=2.5 and temperature 60°C according to test 5 reaction conditions. Due to the small particle size and high surface area of the powder, the particles tend to accumulate.

3.7. *Printed conductive patterns on glass substrate.*

In the case of dough silver nanoparticles ink, the presence of the residual organic stabilizers such as polyvinylpyrrolidone or other non-volatile components has a negative impact on the resistivity of printed patterns. These residuals prevent the contact of particles with each other, resulting in low electrical conductivity of the printed pattern.

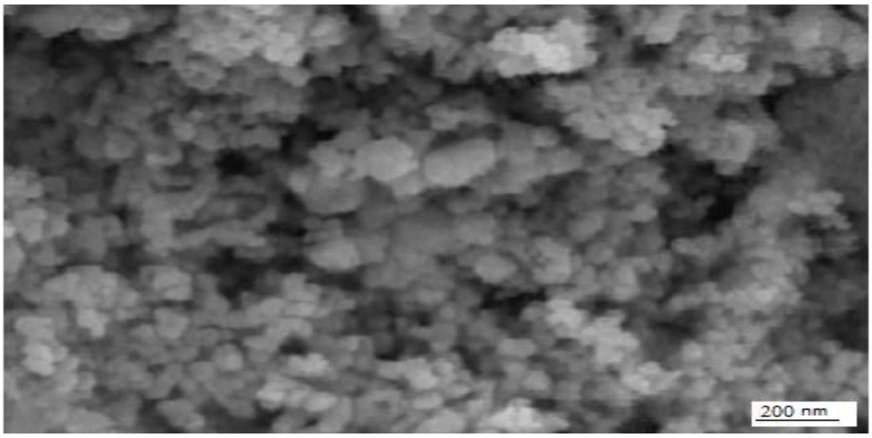

Figure 6. SEM micrograph of Ag NPs produced from test 5.

In this study, the PVP in the Ag nanoparticle suspension was washed many times to remove it almost completely. Usually, the metal nanoparticle suspension contains surfactants such as PVP [18] which tends to diminish the conductivity of the printed metal layer [19]. Then, the film conductivity is sensitive to the amount of PVP residue. For example, by reducing the amount of PVP to 5 wt. %, the resistivity of the film printed using the ink of Ag nanoparticles could be improved to 16μΩcm only after thermal annealing at 260°C [19]. So, after the printing of the pattern, it is essential to cure the layer in order to remove excess solvent and PVP from the surface of Ag NPs and increase the conductivity of the silver ink. The Ag NPs begin to melt and contact with each other to form conductive paths. Figure 7 shows the printed lines of silver ink on glass substrate. The droplets coalesce into a continuous pattern of substrate indicating that as-prepared Ag inks possess an excellent printability and good adhesion on the glass. Also, the printed pattern was observed by scanning electron microscopy technique to examine surface morphology after temperature treatment at 270°C for 30 min as depicted in Figure 8.

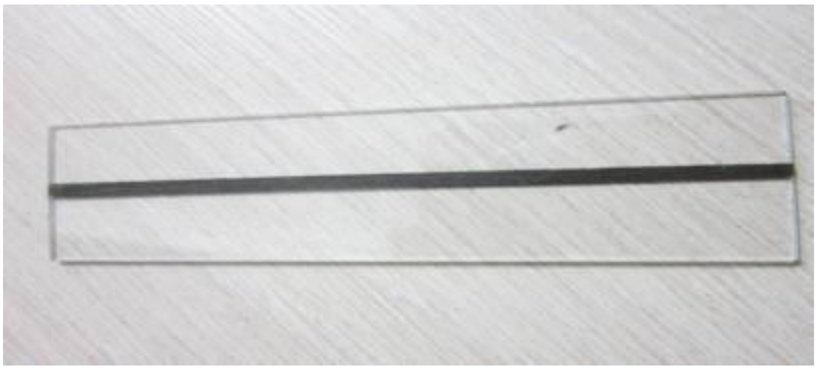

Figure 7. Printed line of silver nanoparticles ink on a glass substrate.

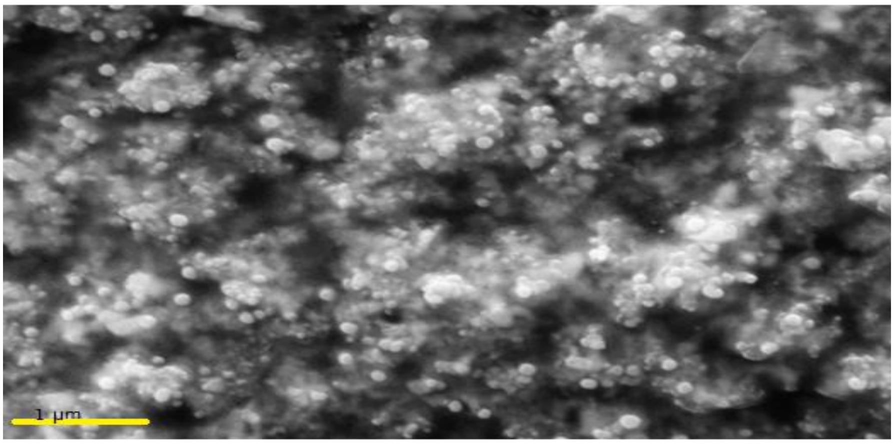

Figure 8. SEM picture of surface morphology after heat treatment at 270°C for 30 min.

The sintering and densification processes directly affect the electrical properties of these films [20]. These patterns were sintered in an oven at 270°C for 30 min under argon environment and the optimal electrical resistivity value (3.1μΩcm) was obtained from experiment 5 (table 3). The resistivity of printed pattern is double the resistivity value of the bulk silver (1.58μΩcm) and these results are in agreementwith Fuller et al. findings [21]. However, a higher sintering temperature could be more effective to decompose high molecular weight materials such as PVP.

Conclusions

In this work, silver nanoparticles were synthesized by reducing silver nitrate with glucose in the presence of protective agent PVP. The addition of sodium hydroxide enhanced the reaction rate. In order to obtain the smallest size nanoparticles, the optimal reaction conditions were PVP/$AgNO_3$ =1.6, Glucose/ $AgNO_3$ = 2.5 weight ratio and the temperature 60°C. Under these conditions, Ag NPs were well dispersed with a size distribution around 40 nm and quasi-spherical shape. Also, the experimental results demonstrated that the PVP as a protective agent plays a decisive role in controlling metallic silver NPs size, size distribution, and particle agglomeration. The resistivity of printed patterns is significantly influenced by the sintering time and the critical curing temperature. So, we have to accurately adoptthe critical sintering temperature.

The printed pattern optimal electrical resistivity of 3.1μΩ.cm was achieved, after optimally chosen reaction parameters, by heat treatment at 270°C for 30 min, this value is about two times more than the resistivity of bulk silver (1.58 μΩ. cm), and it could serve as conducting lines for flexible electronic applications.

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