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Biochemical synthesis, characterization and electrodeposition of silver nanoparticles on a gold substrate

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Abstract

Silver nanoparticles (AgNPs) antibacterial and antimicrobial properties have made them useful in the fields of medicine, for health care, consumer products, industrial purposes and more specifically food packaging industries. Though AgNPs can be synthesized by various methods, the more environmentally friendly option was adopted. Available literature shows that AgNPs can be infused into plastic and polyethylene containers and used for packaging foods and drinks to shield them from fungal or bacterial decay thereby extending their shelf lives. Tests to ascertain the concentration and rate of migration of the AgNPs from the packaging to the food are deemed necessary. In this research *Ocimum gratissimum* (Og) and *Vernonia amygdalina* (Va) silver nanoparticles were biosynthesized, and were of varied sizes with some agglomeration with mean sizes 41 nm and 28 nm, respectively. Their Surface Plasmon Resonance (SPR) occurred in the range 432 nm − 442 nm. Electrodeposition of these nanoparticles on a gold substrate from an acidic medium was done and AFM images show that the Va-silver nanoparticles had small grains and provided a better surface coverage than the larger round flakes of the Og-silver nanoparticles. The nanoparticles were found to have diffusion coefficient values which tallied with their sizes. Thus for the smaller Va-silver nanoparticles it was $1.76 \times 10^{-7}\ cm^2/s$, while for the Og silver nanoparticles it was $3.94 \times 10^{-7}\ cm^2/s$ showing that the migration rate of the Og- silver nanoparticles was higher than that of the Va-silver nanoparticles. Hence for faster nanoparticle migration, the Og-nanoparticles is ideal but for a uniform, and even surface coverage, the Va-silver nanoparticles should be employed.

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1. Introduction

Silver nanoparticles have become popular due to their optical, antibacterial and antimicrobial properties. They are used in electronics [1, 2] as sensors [3], in medicine [4] as drug carriers [5], as coating agents for dressing wounds [6], for food preservation and for treating contaminated water [7]. AgNPs have been used in textiles to kill bacteria and eliminate body odours and can be used for extending the shelf life of fruit juices [8, 9].

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Most recent studies on antimicrobial nanocomposite in food packaging are based on silver nanoparticles and it is reported that using nanoparticles in food packaging industries could tackle the problem of short shelf-life for products that can decay [10, 11].

Silver nanoparticles can be synthesized using chemical methods, but its biosynthesis is more environmentally friendly. [12].The use of leaf extracts is applauded because they have in them stabilizers or capping agents. Biosynthesis also produces biocompatible nanoparticles said to be useful in the field of medicine [13]. For effective application of silver nanoparticles, there is need to develop cheap, eco-friendly methods of synthesizing them and the electrodeposition technique is one of those methods.

Electrodeposition of a metal on a foreign substrate produces a thin film of the metal on the substrate and modifies the surface properties of that substrate and the thin film acquires physical and chemical properties which are different from the bulk of that metal. Electrodeposition technique for nanoparticle production is fast and cheap as reported by Mohanty [14] and improves the electrical properties of nanoparticles [15]. Furthermore; it gets the nanoparticles straight onto the substrates offering effective control of its size, form and structure.

Silver nanoparticles act against pathogenic bacteria and spoilage fungi and can be used in biodegradable and non-biodegradable polymers for making food packages [16] however, a migration test of the silver nanoparticles from the packages to food is of utmost importance and should be done to ascertain if the obtained values fall within the safe limits.

Silver and zinc nanoparticles have been infused into thins films which were used to form polyethylene packaging for storing orange fruit juice. The packaging material was reported to have reduced the pasteurization temperature of the juice, improving on its shelf life [10]. This study reports that though AgNPs are considered safe as far as US food and drug administration is concerned, there is a growing concern about health issues which may be triggered by high intake levels of the nanoparticles as a result of their migration from the packaging to the food they contain. Studies on silver-lined packaging have been done and main concerns were also on the sizes of the nanoparticles as well as its rate of transfer to foods [17]. Another research addressed the migration of silver in the form of nanoparticles into food [18]. The study which investigated four types of plastic containers, reported that concentration and amount of silver which migrated into food content varied from 13 to 42 $\mu g/g$. It was concluded that silver easily migrates into food especially if in contact with acidic substances.

The above review stresses the need to make silver nanoparticles using environmentally friendly methods. It also reports that thin films of silver nanoparticles can be infused into plastics or polyethylene containers used for food packaging. Major concerns in each of the listed cases are the nanoparticles sizes, concentration and migration of the silver nanoparticles from the packaging to the food it contains. In this present research, two species of silver nanoparticles were synthesized using aqueous silver nitrate and two types of plant leaf extracts. In this work, Ocimum gratissimum (Og) and Vernonia amygdalina (Va) plant leaf extracts were used for the silver nanoparticles synthesis. The nanoparticles were characterised using op-

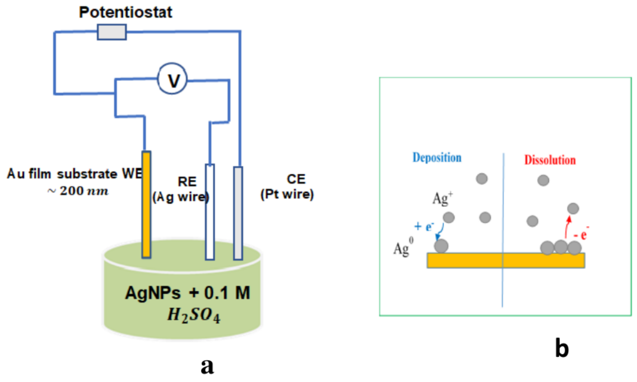


Figure 1: (a) Electrodeposition process of silver from the silver nanoparticles on a gold substrate using a three-electrode cell (b) and the schematic illustration of the stripping process.

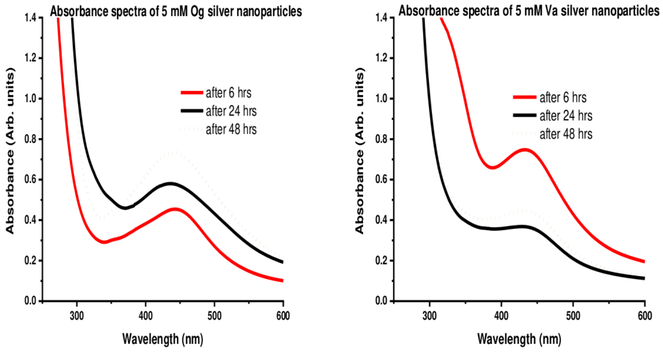


Figure 2: Time dependent UV-Vis absorbance spectra of the Og and Va silver nanoparticles.

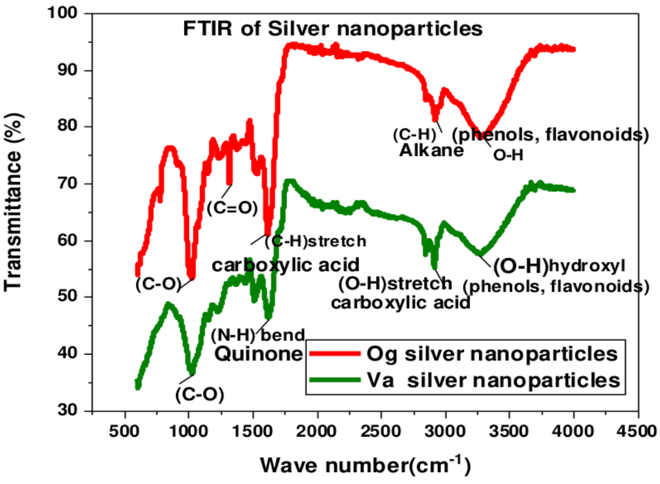
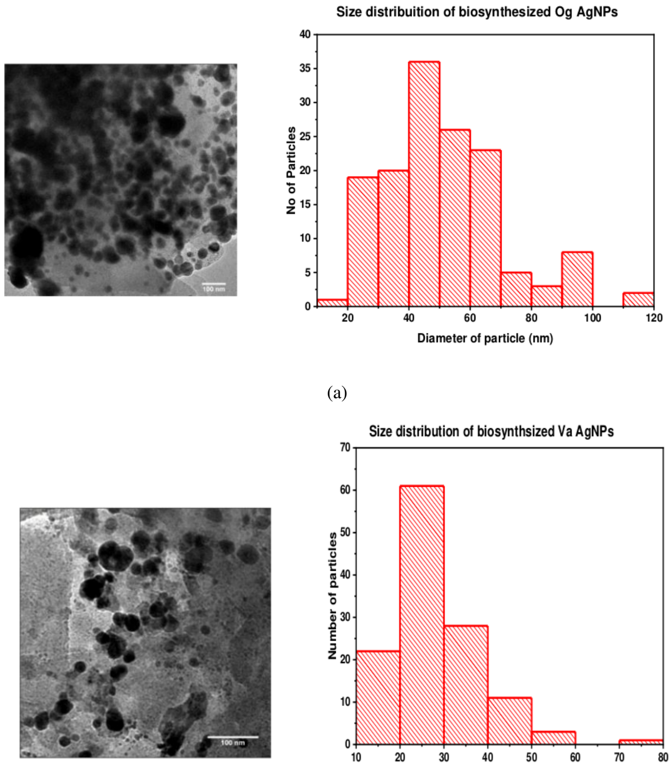


Figure 3: FTIR spectra of the Og- and Va-silver nanoparticles.

Table 1: Variation of Peak current with scan rate for Og-silver nanoparticles

scan rate V/s	$\sqrt{\text{scan rate}}\ (V/s)^{-1/2}$	Peak current i_p (A cm^{-2})
0.01	0.1	0.000422
0.02	0.141	0.000354
0.05	0.223	0.000272
0.1	0.316	0.000184
0.15	0.387	0.000117



(a)

(b)

Figure 4: (a) TEM of Og-silver nanoparticles and the histogram showing size distribution and (b) TEM of Va-silver nanoparticles and the histogram showing size distribution

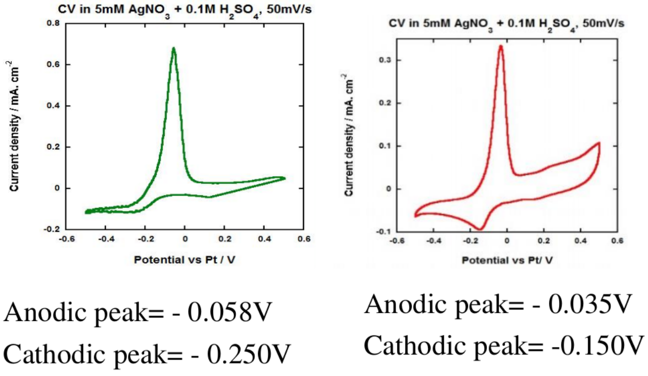


Figure 5: Cyclic voltammograms of the Og- and Va- silver nanoparticles

tical spectroscopy, electron microscopy and by using electrodeposition techniques (Cyclic Voltammetry (CV) and Chronoamperometry (CA). This work did not study the antibacterial or antimicrobial properties of the nanoparticles but rather the behaviour of the nanoparticles in an acidic medium. Furthermore, the sizes, structure, surface morphology, surface coverage abilities and diffusion coefficients of the two silver nanoparticles species were obtained.

2. Materials and Methods

Og- and Va- silver nanoparticles (AgNPs) were synthesized using aqueous and *Ocimum gratissimum* (Og) and *Vernonia amygdalina* (Va) plant leaf extracts as presented by Mfon et al. [18]. The AgNPs were characterised using UV-Vis, FTIR, and TEM. A mixture of 50 ml of the Og- or Va -5 mM silver nanoparticles solution and 50 ml of 0.1 M H_2SO_4 was poured into a three electrode electrochemical cell (Figure 1a) with silver as the reference electrode (RE), platinum as counter electrodes (CE) and “gold-on-glass” as the Working electrode (WE) was used for the experiment.

Platinum wire was chosen as the counter electrode (CE) because it is stable under varying conditions and will not negatively affect coupled redox systems [19, 20, 21]. The working electrode was gold thin films evaporated on glass thermally treated to have the (111) dominant surface orientation [22] and a potentiostat (Bio Logic SP-150 Science instruments) was used for the electrochemical deposition process. All chemicals used were of analytical grade and with $>$ 99% purity and purchased from Sigma Aldrich.

The silver deposition on the gold substrate was done with de-aeration to reduce the background current from oxygen reduction reaction and minimize any interference with the deposition kinetics. The H_2SO_4 acted as the charge bearing group to enhance conductivity and the electrodeposition was done at an assumed temperature of 25 °C [23]. Multistep Chronoamperometry (CA) was used for the deposition of the nanoparticles on the gold substrate and the derived graph was integrated to get Q/A which was substituted in equation (1) to obtain the film thickness for different deposition times t. The thin films of the silver nanoparticles electrochemically deposited on a gold substrate was scanned using the Nanosurf Easyscan 2 AFM and the tapping mode was employed to avoid destroying the surface of the thin films. The probe tip used was NCLR and with its voltage set at 1V and free vibration amplitude at 200 mV, the surface morphology of the silver nanoparticles deposit on the gold surface was studied. The average thickness of the silver film deposits on the gold (from the electrolyte) for varying deposition times: 5, 10, 20 and 30 mins was calculated using equation (1).

The thickness of the silver (deposit) film is:

$$T = \frac{QM}{zF\rho A}. \tag{1}$$

Q/A = charge per unit area derived from the integration of the Chronoamperometry (CA) graph, $z = 1$ because one electron is involved in the reaction), F = Faraday's constant (9.6×10^4), ρ = density of silver 10.5 g/cm^3, $A = 0.98\ cm^2$.

Cyclic voltammetry (CV) of Pt/Ag$^+$ on gold electrode for bulk deposition of the silver nanoparticles was studied. The CV of the Og and Va silver nanoparticles (AgNPs) was done in the range +500 mV and -520 mV. The cathodic peak due to the reduction of the silver and the diffusion of the AgNPs to the gold electrode as well as the anodic peak attributed to the stripping of the electrodeposited silver from the gold surface were noted.

With different scan rates ranging from 10 mV/s to 150 mV/s the variation of the oxidation/reduction peak potentials with the peak height of the current density for each scan rate was also noted. From the obtained data, a graph of i_p against $v^{1/2}$ was plotted and the value of the slope was substituted into equation 2 (Randles-Sevcik Equation with an assumed temperature of $25°C$) and the diffusion coefficients of the two species (Og-AgNPs and Va-AgNPs) under investigation were determined.

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2} \tag{2}$$

where i_p = the peak current in amps, n = the number of electrons transferred in the redox event (usually 1), A = electrode area in cm^2, D = diffusion coefficient in cm^2/s, C = concentration in mol$/cm^3$, v = scan rate in V/s.

3. Results and discussion

The UV-Vis absorbance spectra (Figure 2), shows that the Surface Plasmon Resonance for the Og- silver nano-particles occurred between 440 nm and 442 nm while that for the Va- silver nanoparticles was between 432 nm and 438 nm. The FTIR scan of the silver nanoparticles (Figure 3) done in the range 600−4000 cm^{-1} identified the O-H functional group which represents flavonoids and phenols which may have aided in the nanoparticles synthesis. Other functional groups present include the O-H stretch for carboxylic acid and C-H for alkane.

The TEM images show silver nanoparticles of a wide range of sizes with some agglomeration. The size distribution for the two AgNPS species is as shown on the histograms. For the Og silver nanoparticles, the mean size was calculated to be 41.4 ± 0.02 nm while that for the Va silver nanoparticles was 28 ± 0.01 nm (Figures 4a and 4b).

The CV done in the range +500 mV to -550 mV (Figure 5) showed that the difference between the anodic and cathodic peaks for both samples ΔE was minimal and confirmed the reversibility of the process. For the Og silver nanoparticles, the anodic and cathodic peaks were found to be -0.035 V and -0.150 V while that for the Va silver nanoparticles, they were -0.058 V and -0.250 V, respectively.

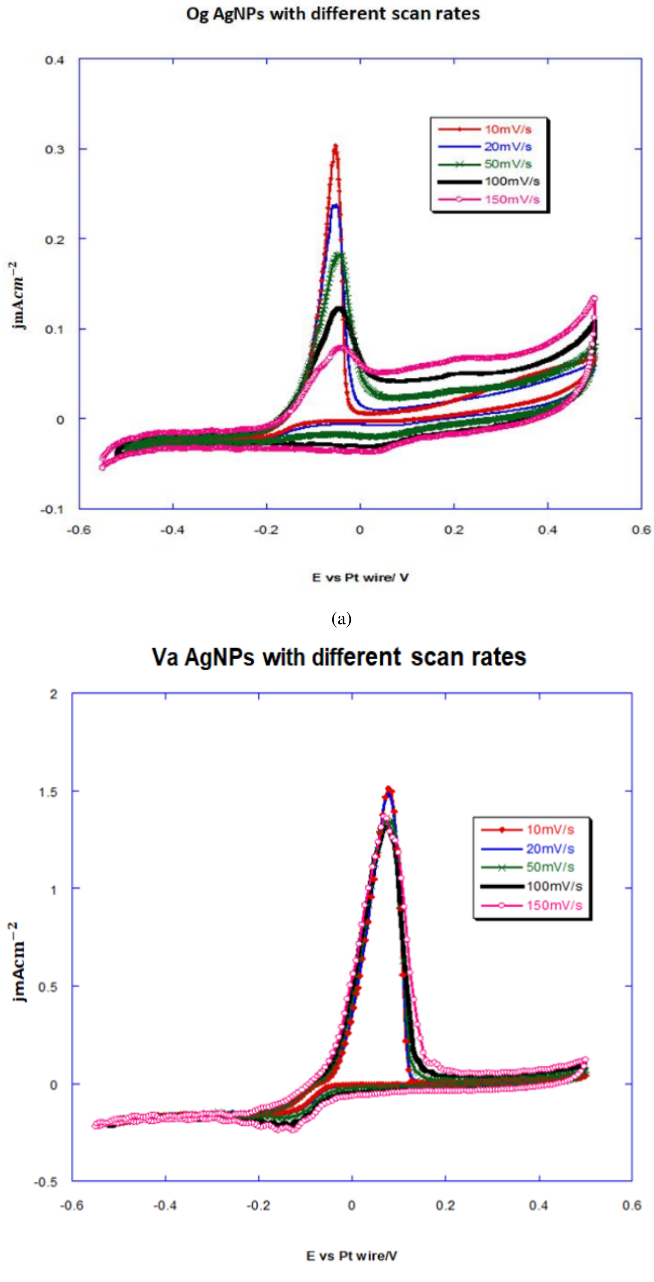


Figure 6: (a) CV of Og-AgNPs with different scan rates (b) CV of Va-AgNPs for different scan rates

The Cyclic Voltammetry (CV) scan of the electrolyte (AgNPs +0.1M H_2SO_4) from 10 mV/s to 150 mV/s (Figures 6a and 6b) shows that for the Og AgNPs, the shift of the peak potential was almost 20 mV with the lowest scan rate producing the high est current density. For the Va silver nanoparticles, the CV scan showed that the process was reversible but with very

Table 2: Variation of Peak current with scan rate for Va-silver nanoparticles

scan rate V/s	$\sqrt{\text{scan rate}}$ $(V/s)^{-1/2}$	Peak current i_p (A cm^{-2})
0.01	0.100	0.001513
0.02	0.141	0.00145
0.05	0.223	0.00140
0.10	0.316	0.00134
0.15	0.387	0.00131

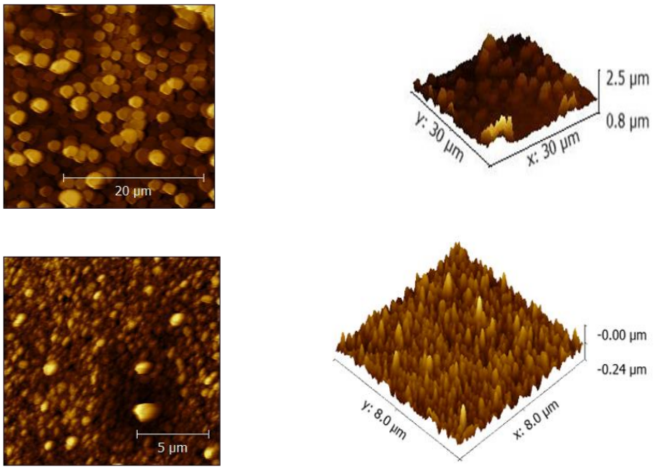


Figure 7: Surface morphology of the deposited silver nanoparticles and the 3D images of the silver nanoparticle deposits on the gold .

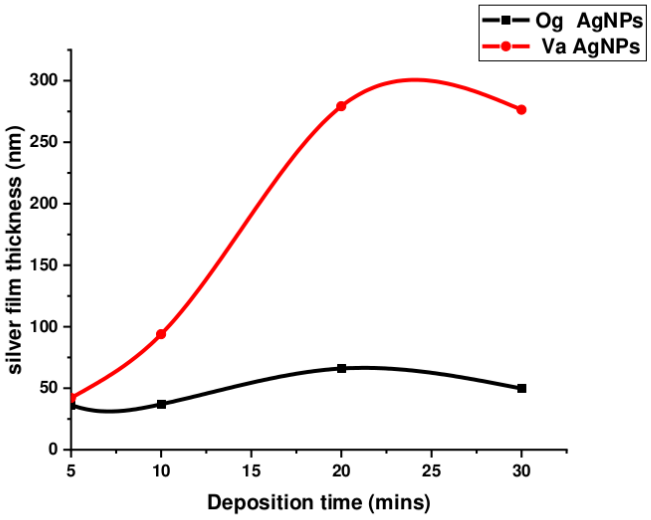


Figure 8: Thickness of the Og and Va silver nanoparticles with time on the gold electrode

insignificant changes in the peak current height with scan rate with the 20 mV/s scan rate producing the highest peak current.

The slope of the i_p versus $Vs^{-1/2}$ for the Og-silver nanoparticles is 8.28417×10^{-4} $Acm^{-2}Vs^{-1/2}$ while that for the Va-silver nanoparticles is 5.542×10^{-4} $Acm^{-2}Vs^{-1/2}$

These results when substituted into equation (2) (Randles Sevcik equation) gave the diffusion coefficient for the Va silver nanoparticles as 1.76×10^{-7} cm^2/s, while that of the Og silver nanoparticles was found to be 3.94×10^{-7} cm^2/s. This shows that the migration rate of the Og-silver nanoparticles was higher than that of the Va-silver nanoparticles.

The AFM images (Figure 7) show the morphology and surface coverage of the silver nanoparticle deposits on gold. The Og- nanoparticles, grains looked like well-defined round flakes though the surface coverage was uneven as the 3D image shows. In contrast, the Va- nanoparticles produced a better and evenly distributed surface coverage with the grains looking like spikes as the 3D image shows. This feature suggests that the oxidation was more anodic for the Va sample. Though the Og AgNPS got loaded on the gold surface, they either got depleted from the electrolyte with time or while covering the surface did not allow more nanoparticles to settle on already deposited ones leading to a halt in further deposition. The z-height of the Og- sample was also found to be higher than that of the Va-sample (Figure 7).

The thickness of silver film that was deposited on the gold substrate with time was found to increase steadily with time until saturation was attained after a self-limiting time of 20 mins for both nanoparticles (Figure 8). For the Og-sample, it is either that the nanoparticles in the electrolyte solution were depleted and further deposition of the Og-silver nanoparticles was halted or an electrochemical oxidation of the AgNPs caused a decrease in particle loading on the gold substrate. This was in contrast to the Va-silver nanoparticles whose deposition continued steadily to a maximum value after 30 mins.

4. Conclusion

Og- and Va- silver nanoparticles were biochemically synthesized and characterised. The Og-nanoparticles had a mean size of 41 nm, with SPR at 440 nm-442 nm, while the Va-nanoparticles had a mean size of 28 nm with SPR at 432 nm – 438 nm. When electrodeposited on a gold surface from an acidic H_2SO_4 medium, it was discovered that the smaller Va-silver nanoparticles though with a lower diffusion coefficient (1.76×10^{-7} cm^2/s) provided a better surface coverage than the larger Og-silver nanoparticles whose surface coverage was uneven, and diffusion coefficient higher (3.94×10^{-7} cm^2/s). The Og-nanoparticles poor surface coverage was attributed to either its electrochemical oxidation during its migration to the gold substrate or its depletion from the electrolyte solution during the electrodeposition process. Conversely the smaller size of the Va- silver nanoparticles may have been beneficial to its observed better surface coverage. Thus if larger grains are desired, Og- silver nanoparticles should be used but for smaller, well- packed grains, the Va- silver nanoparticles should be employed. Furthermore, the Og-silver nanoparticles are best suited for work which requires fast AgNPs migration while the Va-silver nanoparticles should be used where a slower nanoparticle migration is needed.

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