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Synthesis, Characterisation and Zeta Potential of Silver Nanoparticles

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ABSTRACT: Most nanoparticle researches dwell on its antimicrobial and antibacterial properties whereas its sizes and zeta potentials are also important parameters to study for possible nanoparticle applications. Nanoparticle stability in colloids, suitability for use in suspensions and emulsions , ability to fight aggregation, usefulness in drugs to enhance drug loading, release or drug delivery efficiency are predictable if their sizes and zeta potentials are known. This research studied the sizes, zeta potentials, thin film morphology, thickness and surface coverage abilities of silver nanoparticles (AgNPs) synthesized using Ocimum gratissimum (Og) and Vernonia amygdalina (Va) plant leaf extracts. FTIR results show that phenols, flavonoids and some reducing sugars aided the nanoparticles synthesis. The Surface Plasmon Resonance peak wavelength was in the range 435 nm - 451 nm for the Og-AgNPs but 426 nm - 441 nm for the Va- AgNPs. The nanoparticles had negative zeta potentials which varied with the precursor concentration and nanoparticles sizes. Og-silver nanoparticles zeta potential decreased with increased nanoparticle sizes and concentration of the precursor while the Va-silver nanoparticles sizes and zeta potential decreased as the precursor concentration increased. The Og-AgNPs zeta potentials ranged from – 15.03 mV to – 20.3 mV while that of the Va- AgNPs was from – 23.41 mV to – 27.23 mV. This range of zeta potentials indicates some instability and shows that the nanoparticles were in the threshold of agglomeration and could support stabilization but may not favour protein absorption from drugs. While the thin films of the Og-silver nanoparticles comprised of disc-shaped grains unevenly stacked on the gold substrate, that of the Va-silver nanoparticles were smaller spike-like grains. The Og- AgNPs film thickness was 9.4 nm while that of the Va- AgNPs was 10 nm.

Keywords: Silver nanoparticles; Nanoparticle stability**;** Zeta potential; Surface Plasmon Resonance; agglomeration

I. Introduction

The biosynthesis of nanoparticles has in recent times received high acceptance because it is fast, eco-friendly, cost effective, most of the time a single-step process [1] and though nanoparticles can be synthesized using microorganisms such as algae, bacteria, and yeast etc, more researches have shifted to the use of plants and specifically their leaf extracts. This preference is due to the fact that plant leaf extracts have inherent biomolecules which can stabilise nanoparticles, cap them to discourage agglomeration [2] and minimize

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toxicity [3], [4]. Silver nanoparticles (AgNPs) are studied because of their size and shape dependent properties and being good light absorbers and dispersers, their surface Plasmon resonance can be tuned for many applications. Furthermore, silver nanoparticles are useful antimicrobials [5] and have been used for drug delivery [5], [6] and in textiles for odour control [5]. Silver nanoparticles have good electrical and thermal conductivity so might be beneficial in Nano-circuitry and non-linear optics [7]. Many explanations on nanoparticle formation have been given with one asserting that flavonoids with their OH group get changed from the enol-form to the keto-form, giving out a reactive hydrogen atom which reduces the metallic ion into nanoparticles [8].

Zeta potential deals with the net surface charge which nanoparticles possess and gives the measure of the stability of a colloidal solution [9]. Zeta potential is used for effective preparation of suspensions, emulsions and protein solutions and can be used to predict the interaction of particles with surfaces to maximise thin film coating formation. The control of the size and zeta potential of nanoparticles is valuable for effective use of nanoparticles for drug delivery [10], [11], [12]. Furthermore, zeta potential affects nanoparticle adsorption unto a surface as well as its ability to permeate membranes therefore can be used for predicting emulsion instability [13]. The zeta potentials of nanoparticles can also indicate how well it can fight aggregation [14-15].

Previous studies on silver nanoparticles made with 5 mM aqueous $AgNO_3$ and Ocimum gratissimum leaf extract reports that they were crystalline in nature after 24 hrs and showed SPR at 447 nm [16]. The nanoparticles which were of sizes 6 – 33 nm with zeta potential 22.4 mV, had strong surface charges but showed no agglomeration. Silver nanoparticles synthesized with Vernonia amygdalina plant leaf extract and reported to be of sizes 2 nm-10 nm with SPR at 430 nm and 465 nm respectively have been used for antibacterial studies [17] and the focus was just on their efficacy on selected bacteria and pathogens. The dependence of the zeta potential of silver nanoparticles biosynthesized with microorganisms on pH has been studied [18] however; information on the effect of different precursor concentration on the zeta potential and sizes of silver nanoparticles synthesized with Ocimum gratissimum and Vernonia amygdalina plant leaf extract is scarce. Such information is useful to manufacturers of emulsions for skin care such as cosmetic industries who may want to ascertain the stability of the suspensions or emulsions they create for different skin care creams. Furthermore, pharmaceutical companies who may want to add nanoparticles to protein solutions or drugs may need to have an idea of the range of zeta potentials of the nanoparticles they want to add to specific drugs for effective delivery to specific organs. These reasons among others explain the justification for this present research.

This work therefore characterised biosynthesized silver nanoparticles and studied the relationship between the silver nanoparticle sizes and their zeta potentials and from these, the nanoparticle stability was predicted. Thin film coating of a gold substrate by the silver nanoparticles from an acidic medium was also done using electrochemical deposition in order to know the nature of the film coating produced. It is hoped that this work will add to existing knowledge.

II. Materials and Methods

Silver Nitrate ($AgNO_3$) of molecular weight 169.88 and Purity $>$ 99 % of analytical grade was purchased from Sigma Aldrich and Milli-Q water was used for preparing its aqueous solution. Shade - dried Ocimum gratissimum and Vernonia amygdalina plant leaves were boiled in water to produce the plant leaf extracts required for this work.

Preparation of plant leaf extracts and aqueous silver nitrate solution

Plant leaf extracts of Ocimum gratissimum (Og) and Vernonia amygdalina (Va) were prepared as described by Mfon et al [19]. 5 mM of aqueous silver nitrate solution was prepared by dissolving 0.849 g of silver nitrate salt in 1000 cm^3 of the Milli-Q water and by serial dilution other concentrations of it (2 mM, 3 mM and 4 mM) were obtained.

Silver nanoparticles synthesis

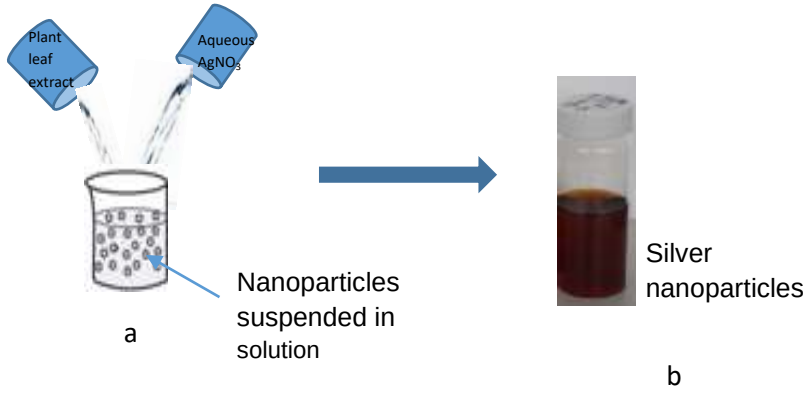

Fig. 1. (a) Silver nanoparticles synthesis (b) sample of prepared AgNPs

To synthesize the silver nanoparticles for each aqueous silver nitrate concentration, 90 ml of each concentration of the silver nitrate was mixed with 10 ml of either Og- or Va- plant leaf extract (Fig. 1) and the mixture was placed in a water bath set to 30 ℃ for 7 hours. A change in the colour of the mixture (aqueous $\mathrm{AgNO_3}$ + plant leaf extract) to a reddish-brown colour indicated the formation of the silver nanoparticles (AgNPs).

Deposition of silver nanoparticles on a gold substrate

A mixture of 50 ml of silver nanoparticles made using the aqueous 5 mM $AgNO_3$ and 50 ml 0.1 M H_2SO_4 was poured into a three-electrode electrochemical cell with silver, platinum, and 'gold on glass' as the reference, counter and working electrodes respectively. At an assumed room temperature of 25 ℃ and using a Bio-Logic potentiostat (SP-150) as described by Mfon et al [20] and multistep chronoamperometry, the electrodeposition of the silver nanoparticles film on the gold substrate was done at the constant potential of $E = -0.4\ V$ for 10 mins (600 s). The thickness of the silver nanoparticles thin film on the gold substrate was obtained using:

$$T = \frac{QM}{zF\rho A} \quad (1)$$

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 is the area of the working electrode available for deposition of the thin film)

The gold substrate on which the silver nanoparticles were deposited was scanned using the Nanosurf Easyscan 2 AFM and the obtained images of the silver nanoparticles deposit on the gold surface are presented (Fig 4).

Characterisation of the silver nanoparticles

The UV-vis absorbance spectra of the silver nanoparticles in solution was obtained after 24 hrs and then after 48 hrs to check for nanoparticle aggregation and stability. This was done using Perkin Elmer Lambda 850 UV-vis spectrometer in the range 200 nm – 800 nm. The FTIR scan of the powder silver nanoparticles was also done using Perkin Elmer 100 FTIR Spectrometer which has an attenuated total reflectance (ATR) module in the wave number range 600 cm^{-1} to 4000 cm^{-1} to identify the functional groups on the AgNPs surface and hence phytochemicals present in the plant leaf extracts used for the AgNPs synthesis. The hydrodynamic diameters of the silver nanoparticles (suspended in solution) as well as their zeta potentials were measured 24 hrs after the nanoparticles synthesis using the DLS Malvern-zetasizer. Thus, 200 μL of the silver nanoparticles solution was mixed with 800 μL of di-ionised water in a beaker and with the help of a syringe the diluted AgNPs was introduced into the disposable folded capillary cuvette (DTS 1070) carefully while ensuring that no air bubbles were trapped in the cuvette. The cuvette was wiped dry, and introduced into the machine for the required measurements. For a measurement, the workspace was changed to reflect which particular measurement was desired, be it the nanoparticles sizes or zeta potential.

FTIR spectroscopy

The FTIR scan of the 5 mM silver nanoparticles (Fig. 2) was done in the range 600 cm^{-1} to 4000 cm^{-1} and gave the identities of the functional groups present on the nanoparticles surface. For the Og- silver nanoparticles among others, the hydroxyl group (O-H) with a broad peak at 3276 cm^{-1} is for flavonoids and phenols; the sharp peak at 2923 cm^{-1} is for Alkanes and the (C-H) stretch at 1615 cm^{-1} is for aldehydes which may have been oxidized to carboxylic acid and reducing sugars. For the Va- silver nanoparticles, prominent peaks observed include the broad peak at 3277 cm^{-1} for the (O-H) group for phenols and Flavonoids, the (C-H) stretch at 2917 cm^{-1} for Alkanes and the peak at 1625 $cm^{-1}$for the functional group (N-H) bend is for Quinone. For both the Og- and Va- silver nanoparticles, the sharp peak at 1030cm^{-1} is for the (C-O) stretch for Esters. It therefore means that the reduction of the silver ions (Ag^{+}) to silver nanoparticles (Ag^{0}) must have been made possible by the phenols and flavonoids as well as some reducing sugars.

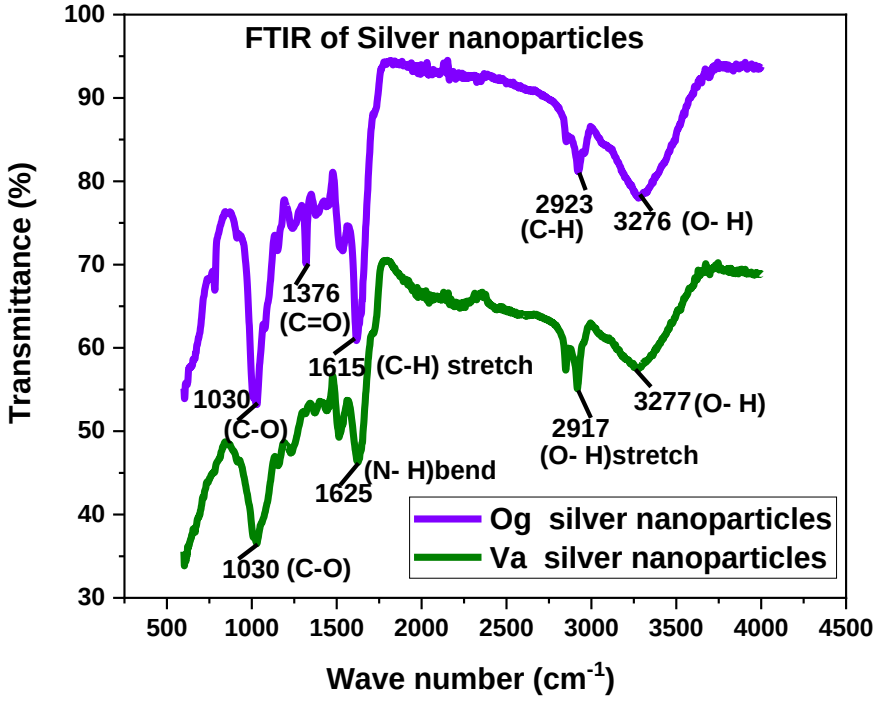

Fig. 2. FTIR scan results of the silver nanoparticles

UV-Vis spectroscopy

As shown in Figs 3 and 4, the surface Plasmon resonance (SPR) absorbance peak changed with time, the concentration of the aqueous silver nitrate solution, and the type of plant leaf extract used. For both the Og- and Va- silver nanoparticles and after 24 hrs, SPR was only observed for the 4 mM and 5 mM nanoparticle solutions. For the Og 5 mM AgNPs, the SPR peak wavelength (λ_{peak}) was 435 nm with absorbance 0.58 after 24 hrs and this increased to 443 nm while its absorbance reduced to 0.46. This range of values agrees with the value reported by Kah & Njobeh [16]. The λ_{peak} for the 4 mM and 3 mM AgNPs after 48 hrs was at 451 nm and while the absorbance for the 4 mM nanoparticle solution was 0.40, the 3 mM nanoparticle solution showed an absorbance of 0.29.

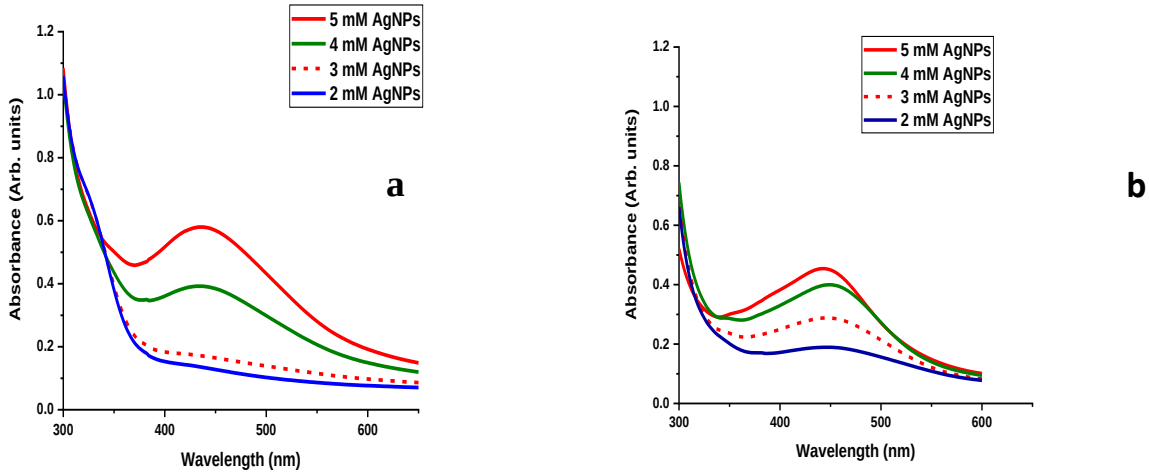

Fig. 3. Time dependent UV-Vis absorbance spectrum for different concentrations of the Og silver nanoparticles (a) after 24 hrs (b) after 48 hrs.

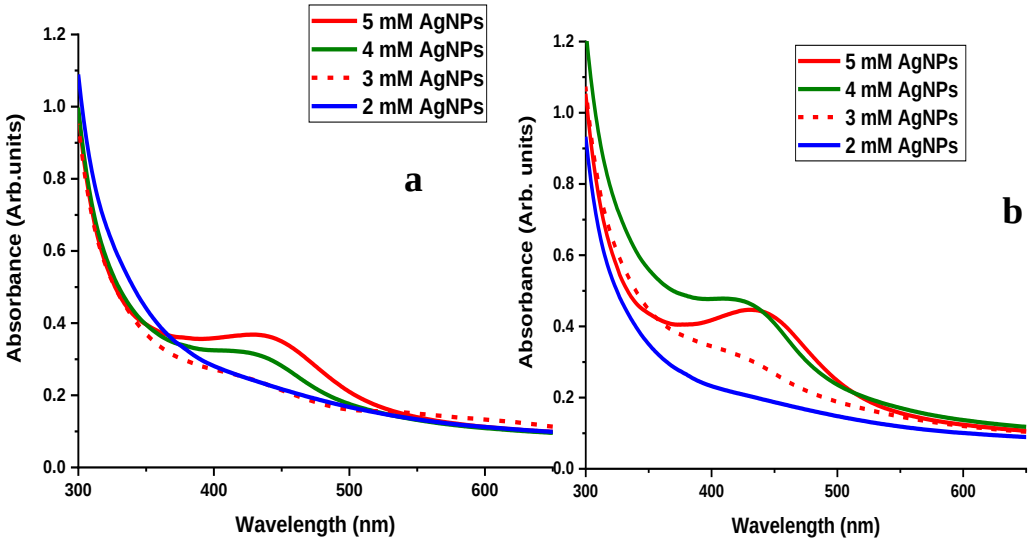

Fig. 4. Time dependent UV-Vis absorbance spectrum for different concentrations of the Va silver nanoparticles (a) after 24 hrs (b) after 48 hrs

For the Va silver nanoparticles, its λ_{peak} increased with concentration of the aqueous $AgNO_3$ used for its synthesis. The λ_{peak} for the 5 mM nanoparticle solution was 441 nm with absorbance 0.37 after 24hrs but this reduced to 438 nm with absorbance 0.44 after 48 hrs. For the 4 mM silver nanoparticles, the SPR wavelength was 430 nm with absorbance 0.31 after 24 hrs and this reduced to 426 nm with absorbance 0.46 after 48 hrs. These results agree with results given by Aisida et al [17] and Nzekekwu & Abosode [21]. A shift in the SPR wavelength to longer wavelengths may be due to aggregation of the nanoparticles while a reduction in the extinction peak indicates instability in the nanoparticle solution. It also implies that the conduction electrons at the nanoparticle surface are delocalised and shared with neighbouring particles resulting in a shift to lower energies and nanoparticle aggregation.

Thin film coating of the gold substrate by the silver nanoparticles

The AFM images (Fig.5) were those of silver nanoparticles made using 5 mM aqueous silver nitrate and each leaf extract in turns. The Og-AgNPs grains are well defined round discs (as shown in its 3D image) which seem to be loaded on top of one another on the substrate. Furthermore, these grains are larger than those of the Va – silver nanoparticles and agree with their measured sizes. The Va-silver nanoparticles on the other hand, had smaller spike-like grains as shown in its 3D image providing in effect a better surface coverage than the Og-silver nanoparticles. This observation agrees with the calculated silver nanoparticles thin film thickness of 9.4 nm and 10 nm for the Og- and Va- silver nanoparticles respectively.

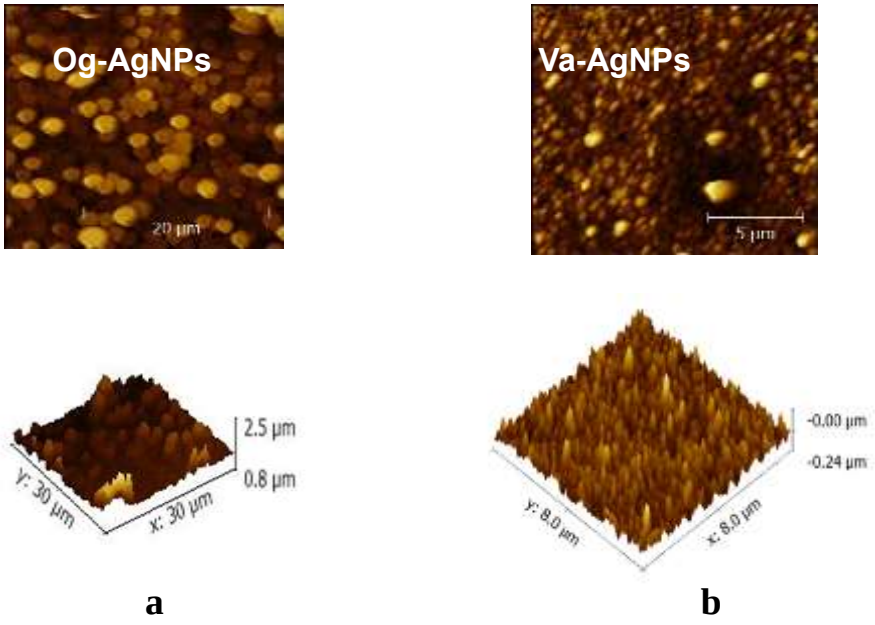

Fig. 5. (a) AFM images of silver nanoparticles deposits on the gold substrate (b) The 3D images of the deposits for silver nanoparticles made with 5 mM aqueous $\boldsymbol{AgNO_3}$ and leaf extracts.

Thin film thickness

By integrating the Chronoamperometry (CA) graph, and by using Eq. (1) the obtained charge per unit area for the Og-silver nanoparticles thin film was $\mathbf{87.82Cm^{-2}}$ resulting in a film thickness of 9.4 nm while for the Va-silver nanoparticles its charge per unit area was $\mathbf{93.70Cm^{-2}}$ and its film thickness 10.0 nm. This shows that the Va silver nanoparticles produced a better surface coverage than the Og-silver nanoparticles.

Zeta potential of the silver nanoparticles

While the Og- AgNPs zeta potential of -20.3 mV is higher than that reported by Kah & Njobeh [16], that of the Va-AgNPs measured as -27.2 mV was a higher negative value. Both the Og- and Va- silver nanoparticles had negative zeta potentials which show that the dispersed nanoparticles in the suspension have negative charges. The zeta potential values of the Og silver nanoparticles which were in the range -15 mV to -20 mV and that of the Va-silver nanoparticles which was in the range -23 mV to -27 mV and both were negative meaning that they are in the threshold of agglomeration, may not likely favour protein absorption from drugs but could support electrostatic and steric stabilization [22], [23], [24].

Nanoparticle sizes and their corresponding zeta potentials

The Og – silver nanoparticles had hydrodynamic diameters (sizes) which increased with the concentration of the silver ions used for their synthesis (Table I) and with their negative zeta potential values. The reverse of the above was observed for the Va-silver nanoparticles whose hydrodynamic diameters decreased with increasing concentration of silver ions used for their synthesis. Furthermore, the larger nanoparticles in the solution/ suspension may be the product of aggregation [25], and will likely have more surface charge than the smaller

nanoparticles. They might flocculate easily and settle on their own in contrast to the smaller nanoparticles in suspension which will require help to flocculate for effective filtration.

Table 1: AgNPs hydrodynamic diameters and zeta potentials(for nanoparticles made with different concentrations of aqueous $AgNO_3$)

AgNPs	Og Silver nanoparticles		Va Silver nanoparticles	
concentration	Sizes (nm)	Zeta Potential(mV)	Sizes(nm)	Zeta Potential(mV)
2 mM	91.28±1.74	-15.03±0.37	116.84±9.65	-23.41±1.55
3 mM	87.13±7.19	-17.14±1.06	97.50±22.45	-23.52±0.69
4 mM	100.89±8.33	-19.26±1.45	75.23±6.21	-23.79±0.92
5 mM	111.27±9.65	-20.30±1.91	64.96±5.36	-27.23±1.91

III. Conclusion

Silver nanoparticles biosynthesized with Ocimum gratissimum and Vernonia amygdalina plant leaf extracts were characterised using optical spectroscopy and electrochemical techniques. The nanoparticles Surface Plasmon resonance (SPR) peak absorbance was dependent on the concentration of the precursor material (aqueous $AgNO_3$), the reaction times of the silver ions with the plant leaf extract as well as the type of plant leaf extract used. The Og- and Va- AgNPs had sizes and negative zeta potentials which varied depending on the silver ion concentration used for their synthesis. While the sizes of the Og-silver nanoparticles increased with its negative zeta potentials and the precursor (aqueous $AgNO_3$) concentration used for its synthesis, the Va-silver nanoparticles sizes reduced as the concentration of the silver ion as well as their negative zeta potentials increased. The AFM images (from electrodeposition) show that the Og-silver nanoparticles had larger disc-like grains which were unevenly stacked on some parts of the gold substrate producing a film thickness of 9.4 nm while the Va- silver nanoparticles with smaller spike-like grains yielded a better surface coverage with a film thickness of 10 nm. The negative zeta potentials of both the Og- and Va- silver nanoparticles are indicators that they have negative charges, while the range of zeta potentials show that they are in the threshold of agglomeration, could support stabilization but may not likely favour protein absorption from drugs.

Declaration of competing interest

The authors declare that there is no competing interest in this work

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