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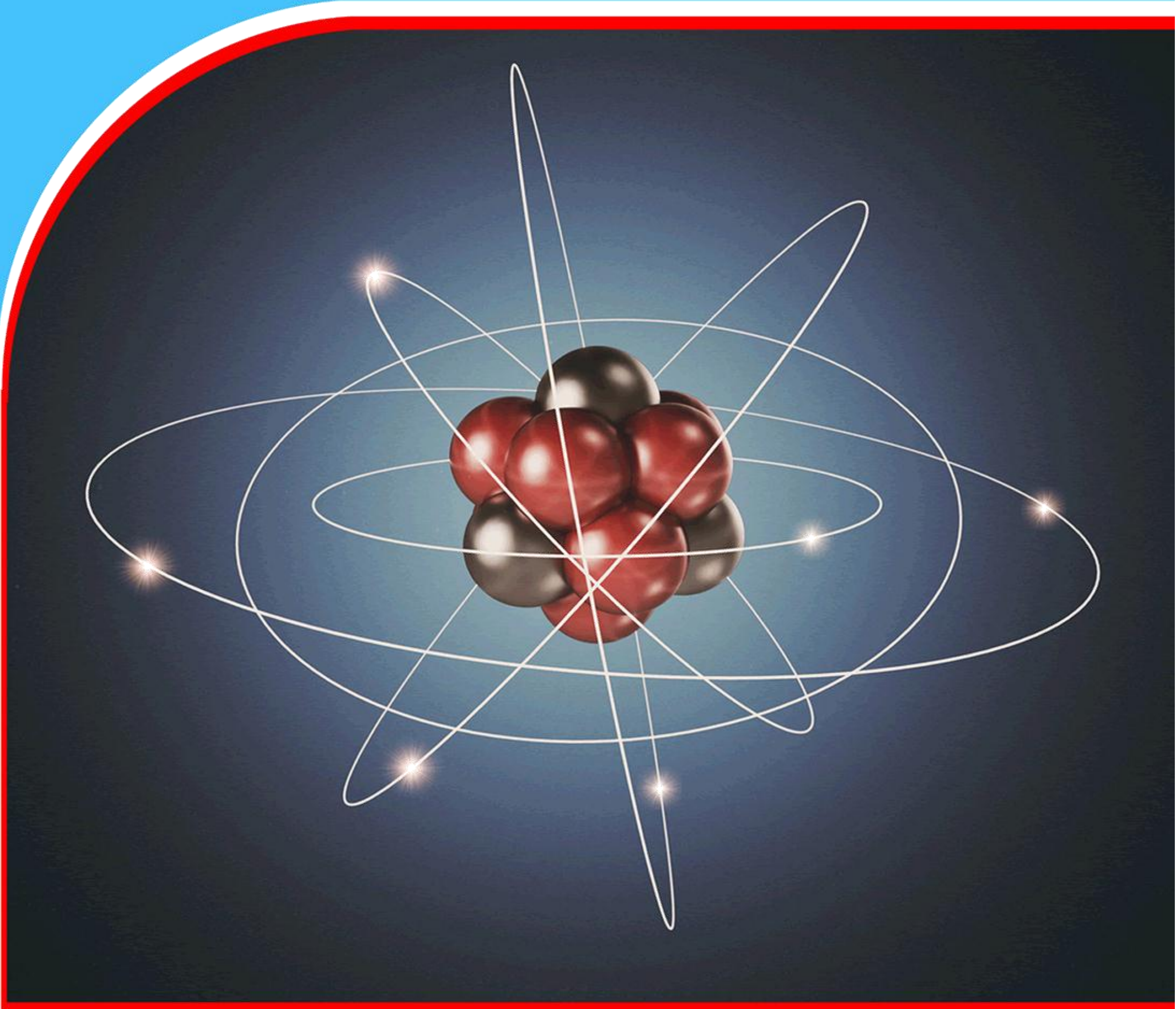

ELECTRODEPOSITION OF SILVER THIN FILMS ON A GOLD SUBSTRATE IN THE PRESENCE OF OCIMUM GRATISSIMUM (Og) AND VERNONIA AMYGDALINA (Va) PLANT LEAF EXTRACTS.

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ELECTRODEPOSITION OF SILVER THIN FILMS ON A GOLD SUBSTRATE IN THE PRESENCE OF OCIMUM GRATISSIMUM (Og) AND VERNONIA AMYGDALINA (Va) PLANT LEAF EXTRACTS.

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Abstract

Electrodeposition an advanced thin film deposition method originally used for decorative purposes and now widely used in industrial applications such as electronics, phonics, magnetic recording and protective coatings, has also been used for the production of size and structure-controlled nanoparticles. In this research, the electrodeposition of silver (Ag) films on gold (Au) substrates with two plant (*Ocimum gratissimum* (Og) and *Vernonia amygdalina* (Va) leaf extracts as additives was explored . The effect of these leaf extracts immediately after addition and after a prolonged exposure in the electrolyte on the silver deposits was studied using cyclic voltammetry (CV), chronoamperometry (CA) and linear sweep voltammetry (LSV). Silver thin films were electrodeposited on gold film from an electrolyte of 5 mM $AgNO_3$ and later 5 mM $AgNO_3$ +0.1 M KNO_3 for 10 minutes, using a double potential step protocol and potentials -0.15 V and -0.3 V with and without the plant leaf extracts. As silver was grown on the gold substrate, silver nanoparticles were also discovered to have been formed in the electrolyte. Though the deposition potential in the presence of the plant leaf extracts affected the kinetics of the silver deposition on the gold substrate, it only slightly affected the silver film thickness on the gold. CV graphs with the plant leaf extracts show lower current densities indicating a slowing down of the deposition/dissolution rates of silver probably due to the adsorption of the leaf extracts on the surface of the growing silver films which may have affected the transport of silver ions (Ag^+) towards the electrode and impacted on the silver deposition/dissolution kinetics. The deposited silver film thickness was 7 nm to 8 nm with the Og leaf extract and 1.5 nm to 2 nm with the Va leaf extract. Atomic Force microscope (AFM) was used for viewing the silver films and the mean grain sizes of the Og silver films was calculated to be$0.87 \pm 0.03\ \mu m$. This was larger than those of the Va silver films calculated to be $0.67 \pm 0.01\ \mu m$. While the Va silver films surface roughness was higher at 10.6 nm, that of the Og silver film was 9.3 nm.

Keywords**:** *Potentiostatic deposition, silver nanoparticles, Ocimum gratissimum, Vernonia amygdalina, cyclic voltammetry, chronoamperometry, adsorption.*

1. INTRODUCTION

Electrodeposition is one of the most advanced thin film deposition methods that have been widely used today in industrial applications such as electronics, phonics, magnetic recording and protective coatings (Schwarzacher, 2006). This technique has also been used for corrosion protection (Alsultani & Tajaldeen (2016), Loto & Loto (2013), and for the production of size and structure controlled nanoparticles (Mohanty, 2011). Electrodeposition, a low-cost method of thin film growth which can be done even at room temperature is characterised by high selectivity and easy scalability to different length scales and can be used for modifying the surface properties of a foreign substrate.

Electrochemical deposition is fast and cheap and has been used for nanoparticle production (Mohanty, 2011). Electrodeposition allows nanoparticles deposit straight unto the substrates and facilitates nanoparticle size, form and structure control. The electrodeposition of solid metal on a substrate can be affected by: the concentration of the metal ions in the electrolyte solution, the nature of the background solution (ion adsorption), the electrolyte solution pH and temperature and sometimes the deposition potential (or current density) – depending on the method of electrodeposition used be it potentiostatic or galvanostatic. The variety of applications of thin films in microelectronics, communication, energy generation and optical electronics explains the current interest in this technique. Furthermore, the formation of silver films and silver nanostructures are of interest because they have been used in medical applications and for food packaging due to the antibacterial properties of silver (Mustatea *et al*., 2015), Istoqola & Syafiuddin, 2020). Electrodeposition of silver from an aqueous solution is done by the application of a constant potential.

This present research used *Ocimum gratissimum* and *Vernonia amgdalina* plant leaf extracts which are antioxidants with reported food and medicinal values (Prabhu *et al*., 2009, Adebolu and Salau, 2005, Bukar *et al*, 2013). The electrodeposition of metals on substrates using plant leaf extracts or fruit juices as additives, is a developing research area and is currently being explored for covering surfaces against corrosion and microbials (Loto *et al*, 2014), Selvi *et al*, 2015), Florence *et al*, 2015), Alsultani and Tajaldeen, 2016). From available literature, it is evident that not much has been done on the effect of plant leaf extracts as additives for electrochemical deposition of silver on substrates and no data are available on the use of the chosen plant leaf extracts (Ocimum gratissimum (Og) and Vernonia amygdalina (Va) for silver electrodeposition on gold. This therefore is what this research will address.

The electrodeposition of silver (Ag) films on gold (Au) substrates in the presence of these two plant leaf extracts was explored. Plant leaf extracts were employed in this electrodeposition because they contain biomolecules such as flavonoids, terpenoids, and polyphenols which can cap the thin film deposits on a substrate preventing its direct contact with the electrolyte thereby reducing metal dissolution (Loto & Loto, 2013). In this experiment, the effect of the plant leaf extracts on the structure of the silver deposits, average thickness of the silver films formed, their resulting surface roughness as well as the grain sizes of the silver deposits and their uniformity were studied. The effect of the applied deposition potential on the average thickness of the silver thin film formed was also studied.

2. METHOD

A three-electrode cell (Figure 1) was used for the potentiostatic electrochemical deposition of silver from an electrolyte of 5 mM $AgNO_3$ with and without a background solution KNO_3 in the presence of *Ocimum gratissimum* (Og) and *Vernonia amygdalina* (Va) plant leaf extracts. To prepare 100 ml of Og or Va leaf extract, 130 ml of deionised water was added to 15 grams of each of the grinded shade-dried Ocimum gratissimum or Vernonia amygdalina leaves and the mixture was boiled for one hour. Thereafter the leaf extract was filtered and stored in a refrigerator for use. The potentiostat used was Bio Logic SP-150 Science instruments. Potassium nitrate (KNO_3) of concentration 0.1 M was used to improve the conductivity of the electrolyte solution and hence the rate of electrodeposition. The electrodeposition was done using a double step potential method at room temperature assumed to be 25 ℃ and at – 0.15 V and later at – 0.3 V potentials. The set up used for the experiment is as shown in Figure 1.

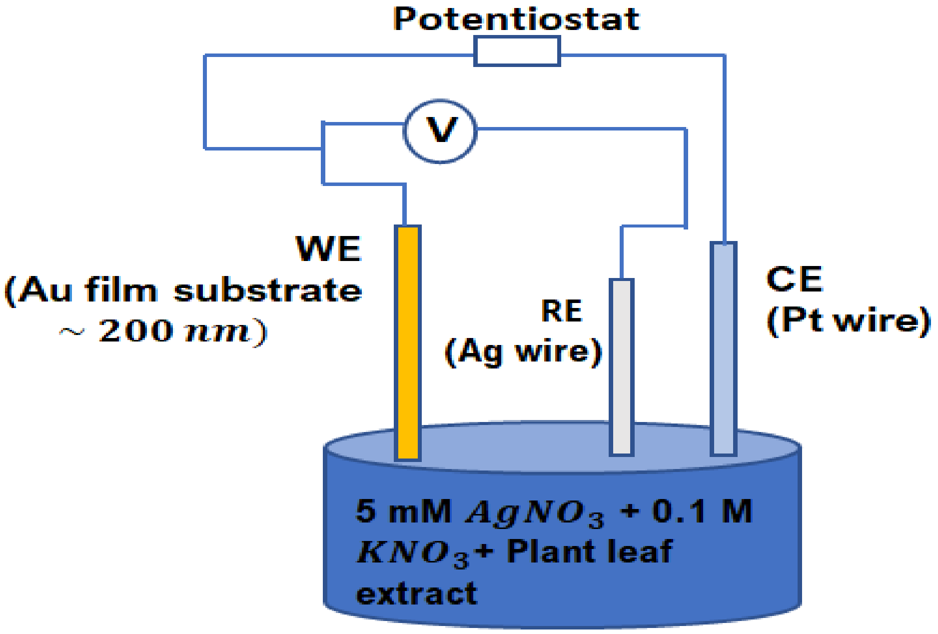

Figure 1: The three-electrode cell used for cyclic voltammetry and chronoamperometry.

The electrolyte was 50 ml solution composed of 45 ml of aqueous $AgNO_3$ (5 mM) and 5 ml of the prepared Og or Va plant leaf extract. Gold films of approximately 200 nm (with 4 – 10 nm Ti adhesion layer) evaporated on glass was the working electrode (WE) used. The area of the working electrode was 0.5 cm^2. This electrode was treated before use by butane flame annealing severally at a height of above 3 cm to remove hydrocarbons which may have been adsorbed on the surface and thereafter its surface cleanliness was confirmed by hydrophilicity test in order to create the (111) dominant surface orientation (Kalska-Szostko, 2012). The reference electrode (RE) was silver wire (pseudo-reference electrode) while the counter electrode (CE) was platinum electrode chosen because of its stability under different conditions as well as its non-interference with coupled redox systems (Kaseem, 2008 & Chen R, *et al*.,2017) .

The reference and counter electrodes were cleaned by immersion in 1:1 mixture of $HNO_3:H_2O$ for 10 secs after which they were rinsed with ultra-pure water and dried with Nitrogen gas. The platinum electrode was further annealed using red-hot butane flame for a few seconds and allowed to cool down before use. The silver electrodeposition on the gold substrate was done in the dark due to the sensitivity of silver to light and the silver deposition was done with de-aeration to minimize the background current from oxygen reduction reaction and check any interference with the deposition kinetics. Techniques employed (Brett & Brett, 1993, Bockris & Khan 1993), were cyclic voltammetry, chronoamperometry and linear sweep voltammetry.

Cyclic voltammetry (CV)

Cyclic voltammetry was done using aqueous solution of 5 mM $AgNO_3$ and later with 5 mM $AgNO_3$ +0.1 M KNO_3 with and without each of the plant leaf extracts at potentials -0.3 V and -0.15 V with a scan rate of 10 mV/s for a range -0.05 V to 0.4 V potentials versus Ag/Ag+ reference electrode. CV of same solution left to age for 90 mins was also explored to see the effect of a prolonged presence of the leaf extract on silver electrodeposition on the gold substrate.

Chronoamperometry (CA)

Chronoamperometry for this work was also done with 5 mM $AgNO_3$ and later with 5 mM $AgNO_3$+KNO_3 solution with and without the plant leaf extracts. By setting the potential initially at $E_1 = 0.3\,V$ for $t_1 = 20$ secs and then stepping to a deposition potential $E_2 = -0.15\,V$ for t_2 =600 secs, later changing to $E_2 = -\,0.3V$ for same time, current-time transients (Figure 5) were derived. The graph for each E_2 potential was integrated and Q_{dep} in each case was obtained. By comparing the charge of dissolved silver with what was deposited, the efficiency of electrodeposition in each case was obtained (Tables 1-3)

Linear sweep voltammetry (LSV)

The LSV dissolution of Ag was done using the set up in Figure 2 and only for potential – 0.3 V in a perchlorate-based solution (1 M $AgClO_4$+0.1 M $HClO_4$) which is free of ions that can adsorb on the surface and the amount of deposited silver was determined. Using a scan rate of 10 mV/s and scanning the voltage from a value $V_1 = -0.005\,V$ close to the equilibrium of Ag, to a more positive potential $V_2 = 0.75\,V > E_{eq}{}^0$ silver dissolution occurred. The resulting LSV graphs are shown in Figure 6.

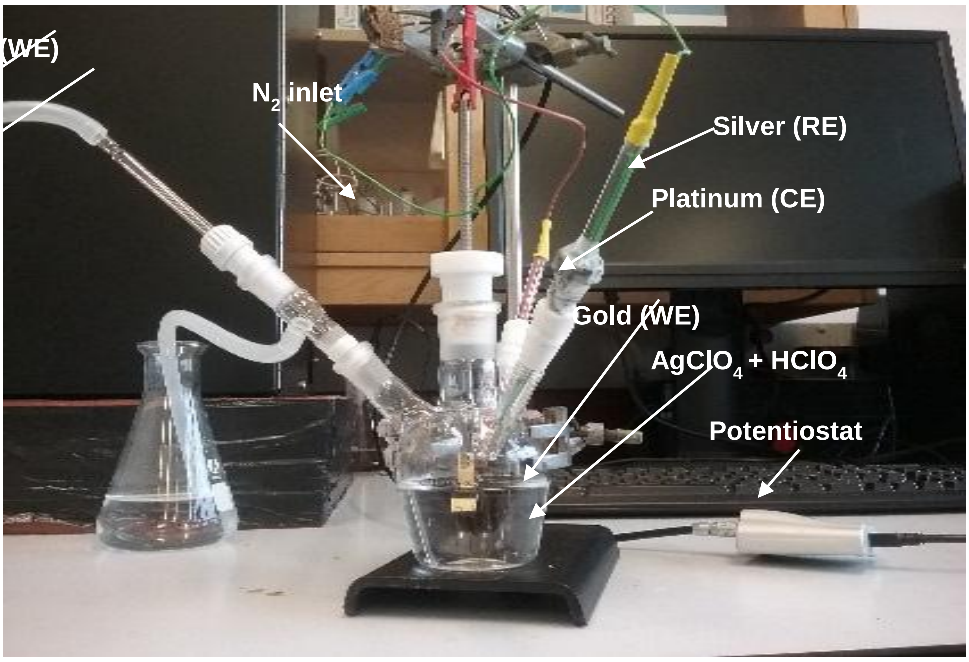

Figure 2: Set up for linear sweep voltammetry.

By integrating the area under the LSV plot, the dissolved charge (Q_{diss}) was derived and by comparing this charge with the charge of deposition (Q_{dep}), the efficiency of the deposition was derived using equation (1)

$$Efficiency = \frac{Q_{diss}}{Q_{dep}} \tag{1}$$

The derived dissolved charge was also used to calculate the equivalent thickness *d* of Ag films deposited on the gold because in conjunction with Faraday's law and under the reasoning that the charge of dissolution (Q_{diss}) is proportional to the mass M of silver deposit. The equivalent thickness of silver films *d* could be calculated using equation (2).

$$d = \frac{Q_{diss}M}{nF\rho A} \tag{2}$$

Where n = no of electrons involved in the reaction ($n = 1$ in this case), F = faraday constant ($9.64\times 10^4 \mathrm{C/mole}$), A is the working area of the substrate ($0.5cm^2$), ρ is the density of silver

Atomic Force Microscope (AFM) characterisation of Ag films

The surface morphology studies of the gold substrate after the silver deposition on it with or without the plant leaf extracts were done using Nanosurf Easy scan 2 AFM. For the scanning of the samples, the dynamic force mode was selected, the NCLR probe tip was used with probe tip voltage set at 1 V and the free vibration amplitude set at 200 mV. The images were of size 5 μm and for silver films made at – 300 mV deposition potential. The images of the silver films were analysed using the Gwydion software which was also used for determining the grain sizes of the silver deposits in each case and their corresponding surface roughness.

3. RESULTS AND DISCUSSION

The CV curves (Figures 3 and 4) show the effects of the added plant leaf extracts as well as that of the KNO_3 background solution. Basically, the kinetics of the silver deposition on the gold substrate was affected. Lower current densities in the CV graphs are indications that both leaf extracts slow down the deposition/dissolution rates of silver probably because of their adsorption on the surface of the growing silver film. With the Va plant leaf extract, the deposition inhibition is reflected in a slightly more negative potential of the onset of the silver deposition.

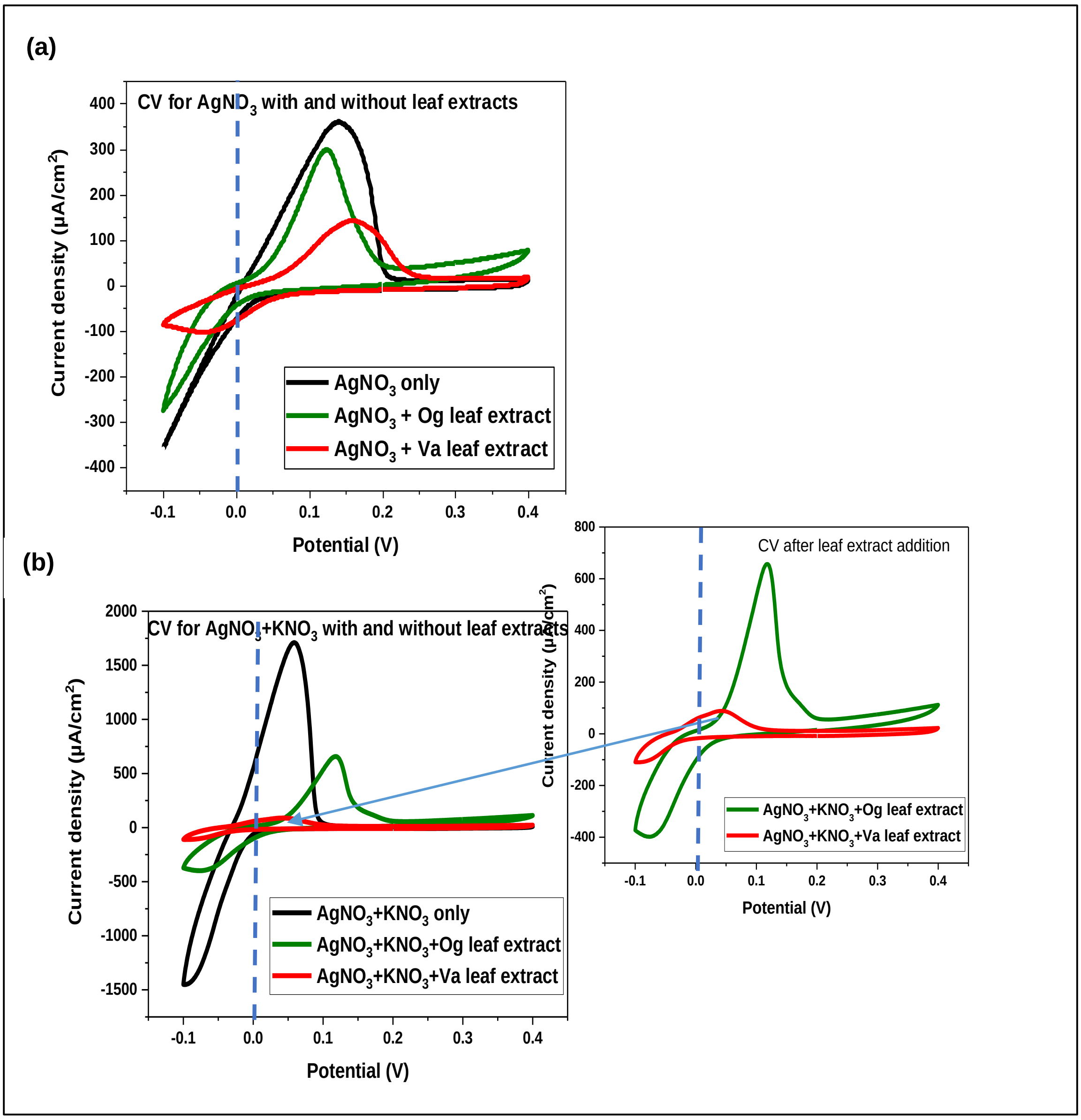

Figure 3: CV plots with and without leaf extracts immediately after leaf extract addition. CVs done in (a) 5 mM $AgNO_3$ and (b) 5 mM $AgNO_3$+0.1 M KNO_3 solution at 10 mV/s. Figure (3b) inset shows enlarged CVs in the leaf solutions for clarity.

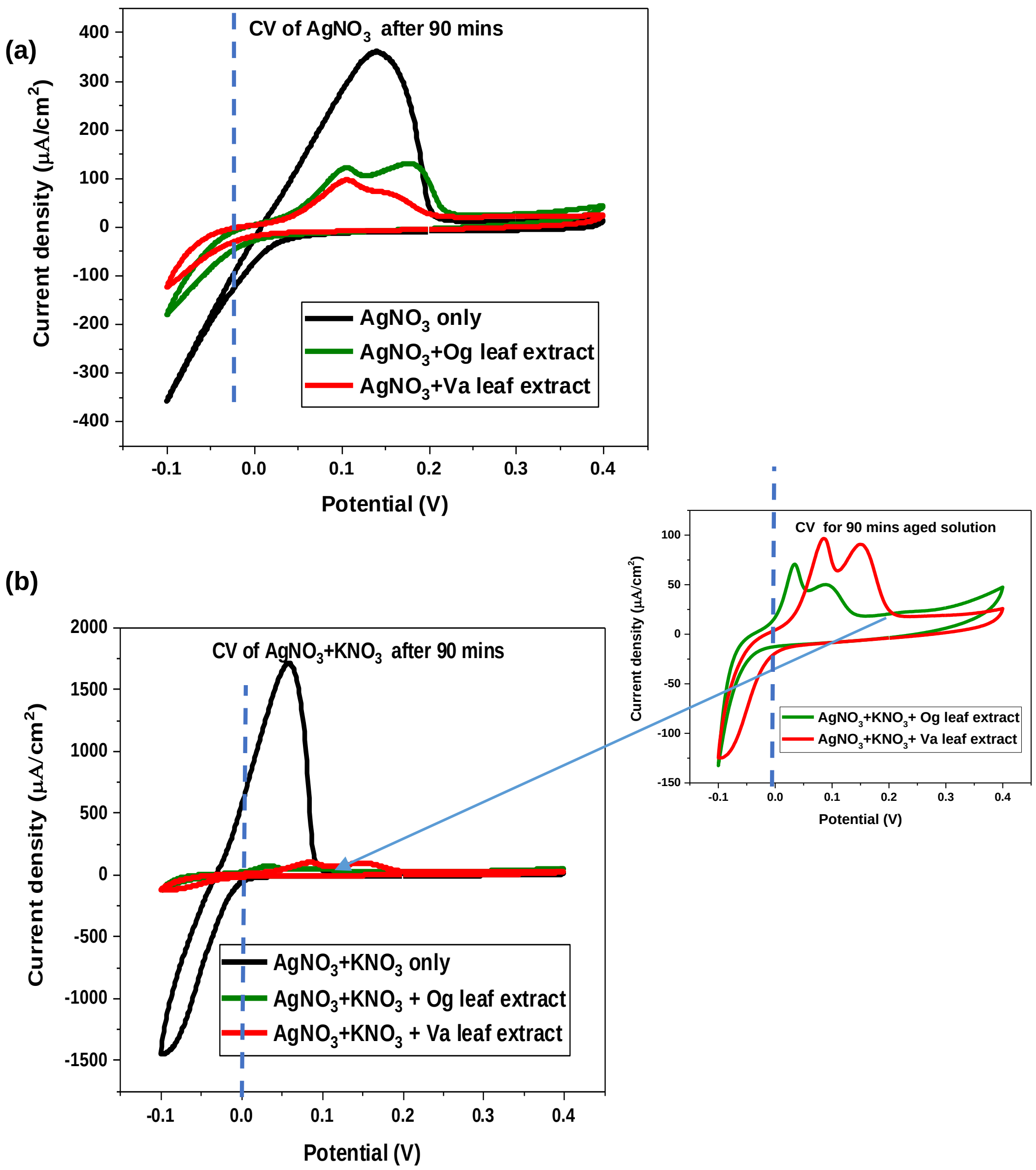

Figure 4: CV plots with and without leaf extracts after ageing for 90 minutes. CVs done in (a) 5 mM $AgNO_3$ and (b) 5 mM $AgNO_3$+0.1 M KNO_3 solution at 10 mV/s. Figure (4b) inset shows enlarged CVs in the leaf solutions for clarity.

For the ageing solution and in the presence of each of the plant leaf extracts, the CV graphs (Figure 4), show two oxidation peaks. It is likely that probably as the silver was being deposited on the gold substrate, silver nanoparticles were simultaneously formed in the electrochemical cell solution and some of these silver nanoparticles may have been deposited on the gold substrate resulting in the depletion of silver meant for deposition and producing in effect reduced silver film thickness as shown in tables 1, 2 and 3.This trend did not change significantly when the deposition potential was changed from – 0.3 V to − 0.15 V.

Table 1: Silver thin film deposition from 5 mM $AgNO_3$ solution with and without the plant leaf extracts at deposition potential of – 0.300 V for 10 mins.

Electrolyte	$Q_{dep}(\frac{mC}{cm^2})$	$Q_{diss}(\frac{mC}{cm^2})$	**Deposition Efficiency** $(\frac{Q_{diss}}{Q_{dep}}\%)$	**Silver film average thickness(nm)**
$AgNO_3$	368	301	82	64
$AgNO_3$+Og	42	33	79	7
$AgNO_3$ + Va	12	11	92	2

Table 2: **Silver thin film after 10 mins deposition from 5 mM $AgNO_3$+0.1 M KNO_3 solution with and without the plant leaf extracts at deposition potential of – 300mV.**

Electrolyte	$Q_{dep}(\frac{mC}{cm^2})$	$Q_{diss}(\frac{mC}{cm^2})$	**Deposition Efficiency** $(\frac{Q_{diss}}{Q_{dep}}\%)$	**Silver film average thickness (nm)**
$AgNO_3$+ KNO_3	245	104	42	22
$AgNO_3$ + KNO_3+ Og	45	31	69	7
$AgNO_3$ + Va	9	8	89	2

Table 3: **Silver thin film after 10 mins deposition from 5 mM $AgNO_3$+0.1 M KNO_3 solution with and without the plant leaf extracts at deposition potential of – 150mV.**

Electrolyte	$Q_{dep}(\frac{mC}{cm^2})$	$Q_{diss}(\frac{mC}{cm^2})$	**Deposition Efficiency** $(\frac{Q_{diss}}{Q_{dep}}\%)$	**Silver film average thickness (nm)**
$AgNO_3$+ KNO_3	195	117	60	25
$AgNO_3$ + KNO_3+ Og	45	38	84	8

$AgNO_3$ + Va	8	7	88	1.5

The CA graphs (Figures 5a and 5b) show the current transients for both -0.15 V and -0.3 V potentials and the changes which occurred were not significant. After 10 mins deposition, the calculated silver film thickness for both potentials were slightly different and the calculated deposition efficiencies were noticed to have improved in the presence of the background solution KNO_3 and each of the plant leaf extracts with the Va leaf extract giving a higher deposition efficiency than the Og leaf extract. Furthermore, the observed current levels were lower and obtained results were in agreement with the effects shown in the CV experiments.

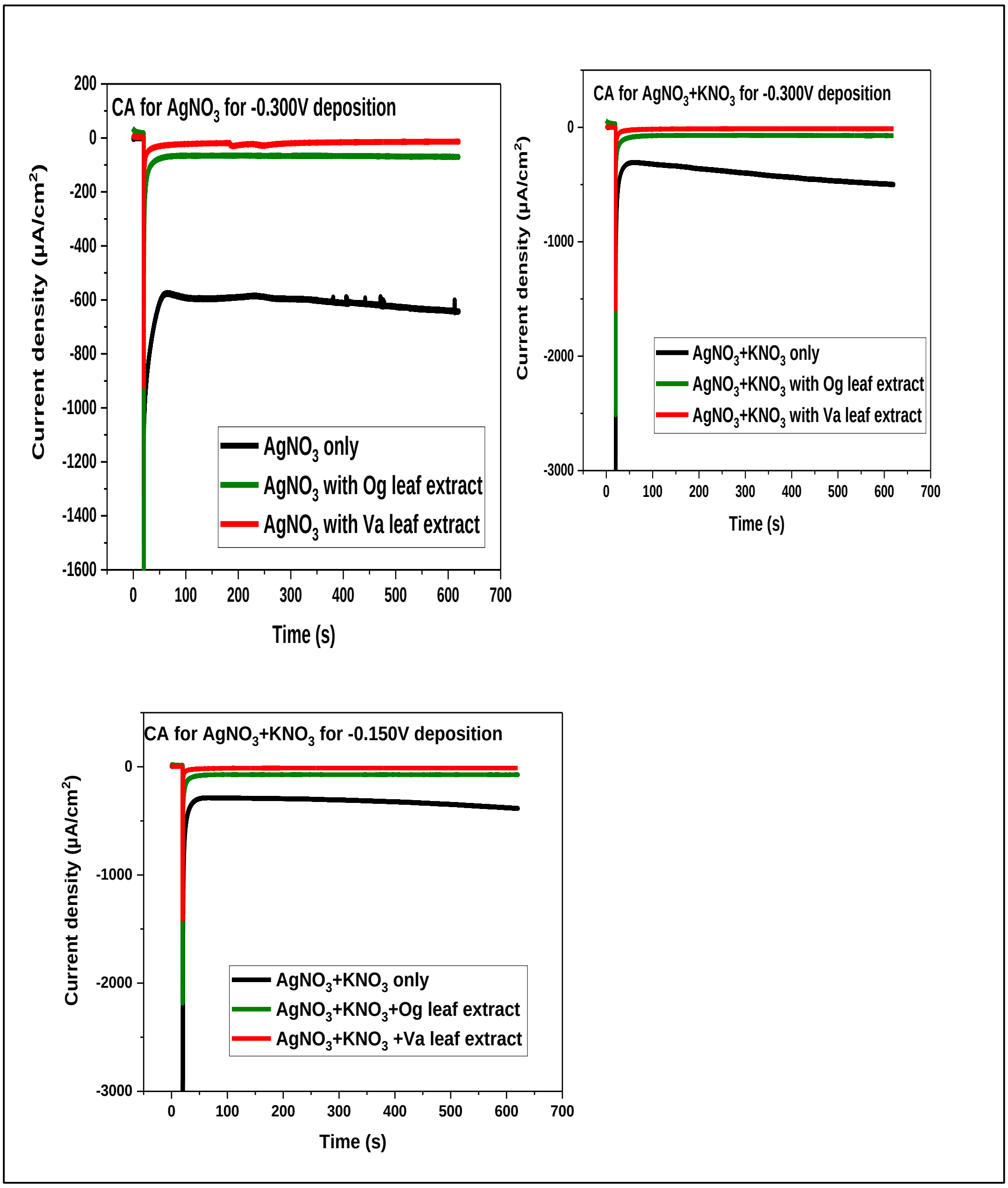

Figure 5(a): CA graphs for silver depositions done at potentials -0.150V and -0.300V for 10 mins in the electrolyte solutions with and without leaf extracts.

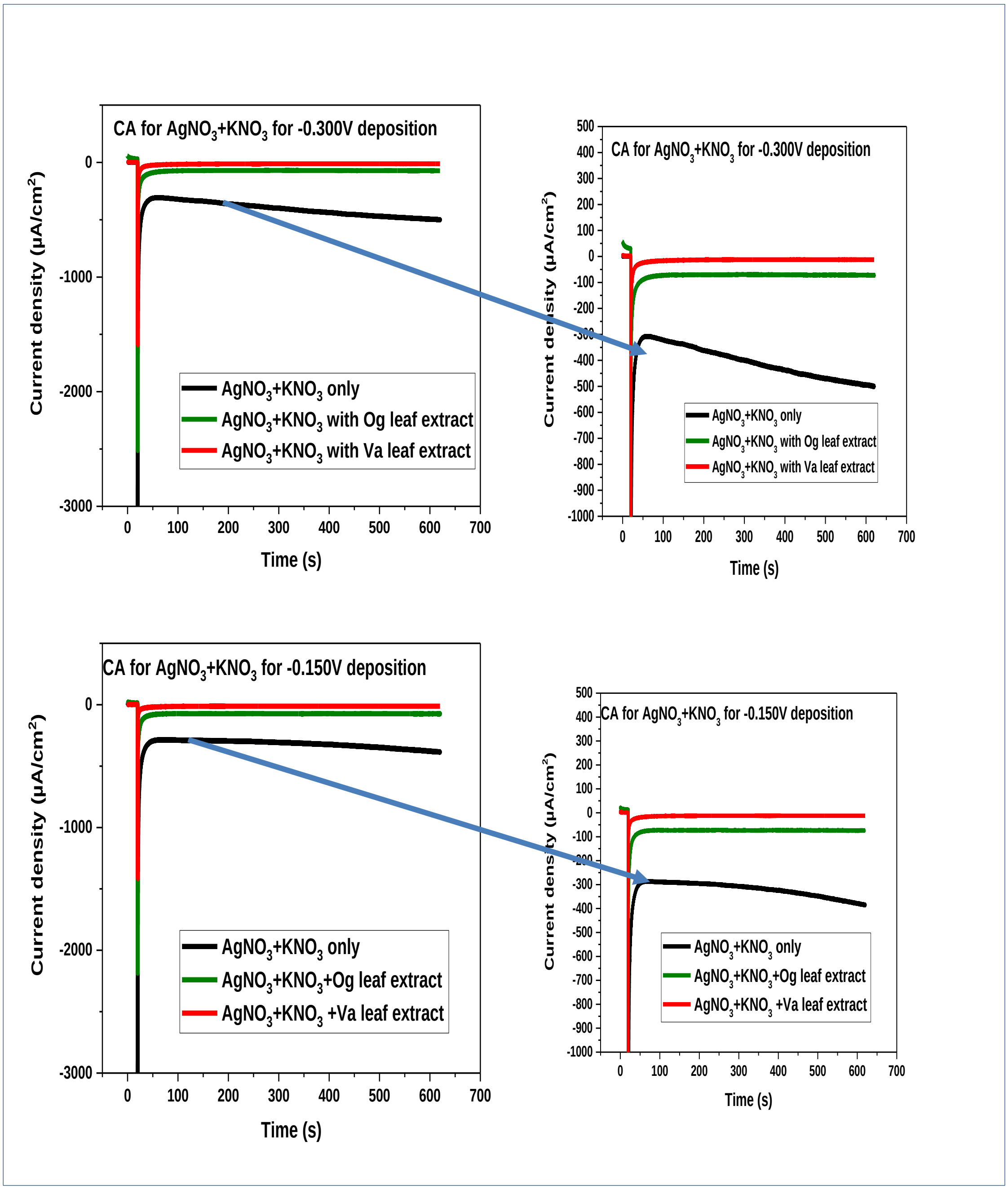

Figure 5 (b): CA graphs for silver depositions done at potentials -0.150V and -0.300V for 10 mins in the solutions with and without leaf extracts with insets showing the current levels in the presence of the leaf extracts were nearly same.

The LSV was done only at – 0.3 V because the CA results showed that the deposition potential did not significantly affect the average silver film thickness. The derived LSV graphs are as shown in Figure 6. The Og plant leaf extract yielded a low amount of silver deposits at potentials close to the equilibrium potential. At this negative potential of – 0.3 V and with the Va leaf extract, a lower silver film deposition on the gold substrate occurred. Corresponding silver film thicknesses in each case were calculated and are as shown in tables 1, 2 and 3.

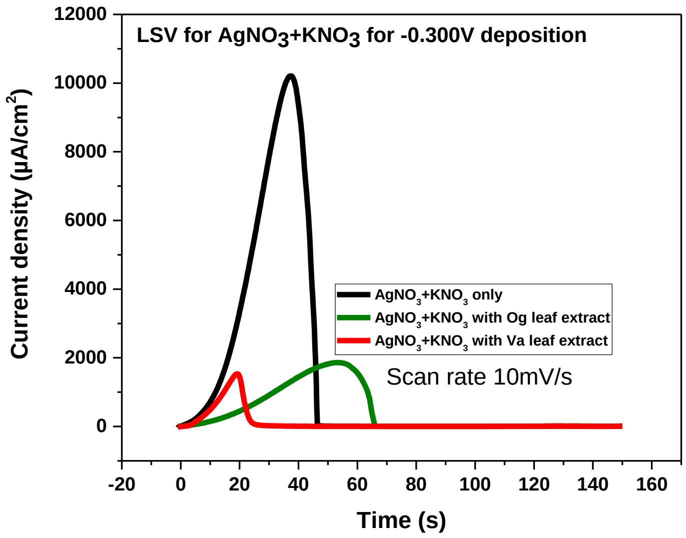

Figure 6: LSV graphs for silver depositions done at -0.300 V for 10 mins.

The morphology of the deposited silver (Ag) films as examined with the AFM is as shown in Figure 7. For silver deposits without the plant leaf extracts, the grains were large and their shapes were not defined. In the presence of the plant leaf extracts, the silver film grains derived from deposition potential – 0.3 V showed refined Og silver grains and the same was the case with the Va silver grains though the Og silver grains were larger $(0.87 \pm 0.04\ \mu m)$ than the Va grains $(0.67 \pm 0.01 \mu m)$. Without the plant leaf extracts, the silver film surface roughness was low at 8.7 nm. While the Va leaf extract produced silver deposits with a higher surface roughness of 10.6 nm, the Og leaf extract silver deposits had a lower surface roughness measured to be 9.3nm.

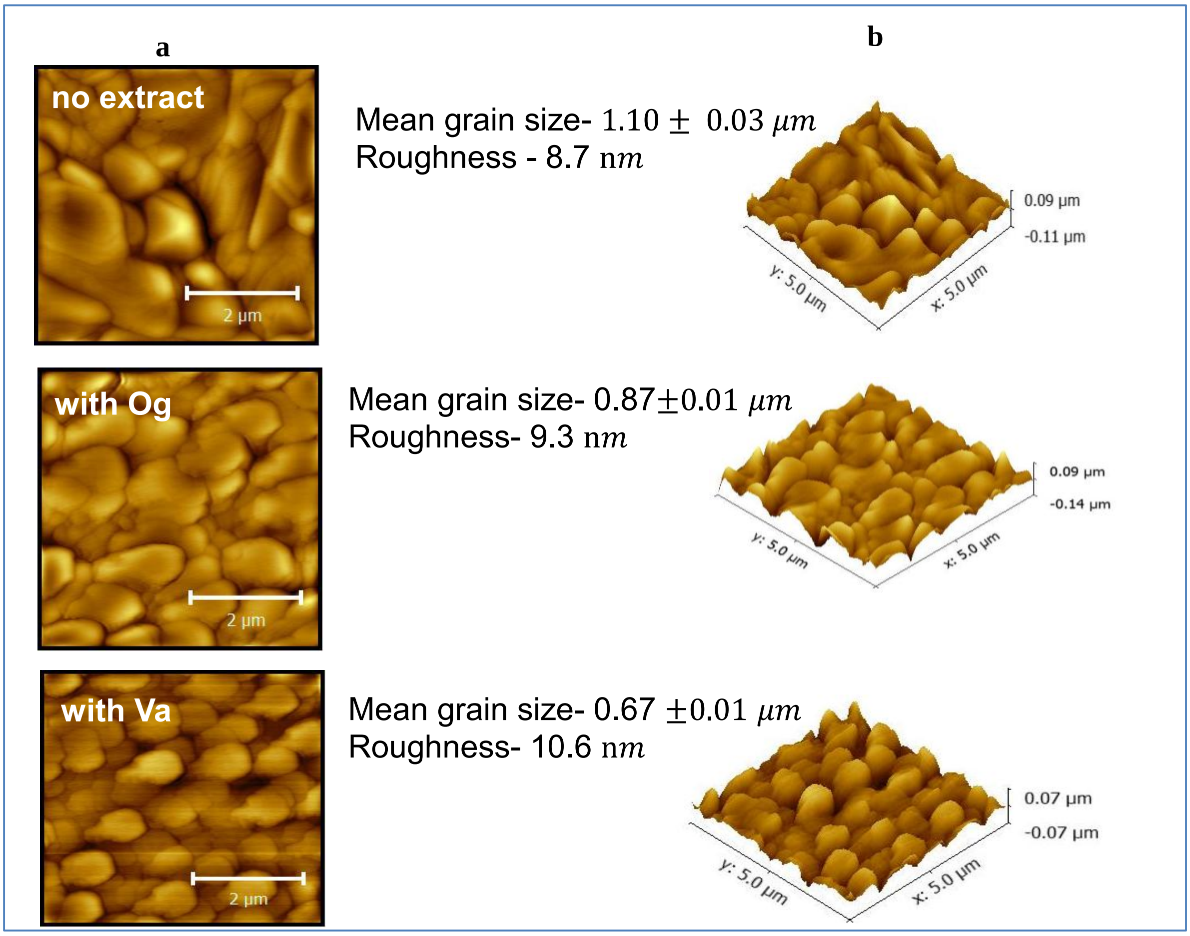

Figure 7: (a) AFM images of Ag films (b) 3D images of the silver grains on the gold from 5 mM $AgNO_3$ at – 300 mV for 10 mins with and without Og and Va plant leaf extracts

CONCLUSION

Silver film electrodeposition on gold film was done using a double potential step method in the presence of *Ocimum gratissimum* and *Vernonia amygdalina* plant leaf extracts at room temperature. The deposition was done for 10 mins from an aqueous solution of 5 mM $AgNO_3$ with and without the background solution KNO_3 or the plant leaf extracts. The obtained results show that the silver film deposition is reduced by the leaf extracts molecules adsorbed on the growing Ag films which in turn affected the rate of electron transport across the surface (activation effect). The produced silver films in the presence of the plant leaf extracts had refined grains whose sizes and surface roughness values which were also leaf extract dependent. Furthermore, silver film deposition efficiency and thickness were enhanced in the presence of the plant leaf extracts with the Og leaf extract giving a higher silver film thickness than the Va plant leaf extract. The deposition potential did not however impact significantly on the silver film average thickness in each case.

The cyclic voltammetry and the chronoamperometry results were in agreement and whether or not the electrolyte solution aged, there was a general effect of the plant leaf extract in the electrolyte solution with an overall effect on the silver deposition/dissolution kinetics. It is possible that the organic molecules in each of the plant leaf extracts interacted with and got adsorbed on the surface of the deposited silver and that their presence around the electrode during the silver film growth may have affected the transport of Ag^+ ions towards the electrode.

Apart from adding to existing knowledge in this field, the results obtained could be used by industries that find them useful. Some modifications of techniques used can also be made to see if better results other than what is reported here can be obtained.

RECOMMENDATION

Greater insight into the behaviour of the ageing electrolyte solution with each of the plant leaf extracts should be sought. For ageing times ranging from 30 mins to 120 mins, the morphology of the silver films produced in each case could be compared with those of silver films produced immediately after leaf extract addition. Moreover, the two oxidation peaks produced during the CV of the aged solution should be investigated.

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