

Preparation of gold, silver and copper nanostructured surfaces by application of a square wave potential regime

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Preparación de superficies nanoestructuradas de oro, plata y cobre mediante la aplicación de un campo de potencial de onda cuadrada

Preparació de superfícies nanoestructurades d'or, plata i coure mitjançant l'aplicació d'un camp de potencial d'ona quadrada

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RESUMEN

Este artículo presenta un planteamiento simple y novedoso para preparar electrodos nanoestructurados de oro, plata y cobre sobre un sustrato de tántalo mediante la aplicación de un campo de potencial de onda cuadrada. El campo de potencial comprende una onda cuadrada cuyo límite inferior de potencial se sitúa en la zona de potencial de la electrodeposición espontánea. La identidad de las estructuras formadas se verificaba mediante EDX y voltametría, mientras que las dimensiones, la forma y la uniformidad de la distribución de las partículas se trazaba mediante microscopía electrónica de barrido. Se averiguaba que las estructuras resultantes dependían de los parámetros de onda cuadrada (frecuencia, amplitud y posición del centro de la onda cuadrada). Las condiciones optimizadas para la fabricación de electrodos nanoestructurados eran una frecuencia de 100 Hz, aproximadamente un periodo de 60 s de aplicación de la onda cuadrada y una concentración 10^{-3} M de los iones metálicos. Por el contrario, tiempos de deposición más largos y mayores concentraciones iónicas daban lugar a la formación de microestructuras tridimensionales.

Palabras clave: aplicaciones de onda cuadrada, electrodeposición, nanopartículas metálicas, superficies nanoestructuradas

SUMMARY

This paper presents a novel simple approach for preparation of gold, silver and copper nanostructured electrodes on a tantalum substrate by application of a square wave potential regime. The potential regime comprises a square wave whose lower potential limit lies within the potential zone of spontaneous electrodeposition. The identity of the formed structures was verified by EDX and voltammetry, while the size, shape and uniformity of distribution of the particles were traced by scanning electron microscopy. The resulting structures were found to depend on the square wave parameters (frequency, amplitude and position of the center of the square wave). The optimized conditions for production of nanostructured

electrodes were a 100 Hz frequency, about a 60 s period of application of the square wave, and 10^{-3} M concentration of the metal ions. In contrast, longer deposition times and higher ion concentrations were found to lead to formation of 3-dimensional microstructures.

Key words: Square wave applications; electrodeposition; metallic nanoparticles; nanostructured surfaces

RESUM

Aquest article presenta un plantejament simple i nou per preparar electrodos nanoestructurats d'or, plata i coure sobre un substrat de tàntal mitjançant l'aplicació d'un camp de potencial d'ona quadrada. El camp de potencial comprèn una ona quadrada el límit inferior de la qual està situat a la zona de potencial de l'electrodeposició espontània. La identitat de les estructures formades es verificava mitjançant EDX i voltametría, mentre que les dimensions, la forma i la uniformitat de la distribució de les partícules es traçava mitjançant microscòpia electrònica de rastreig. S'esbrinava que les estructures resultants depenien dels paràmetres d'ona quadrada (freqüència, amplitud i posició del centre de l'ona quadrada). Les condicions optimitzades per a la fabricació d'electrodos nanoestructurats eren una freqüència de 100 Hz, aproximadament un període de 60 s d'aplicació de l'ona quadrada i una concentració 10^{-3} M dels ions metàl·lics. Per contra, temps de deposició més llargs i majors concentracions iòniques donaven lloc a la formació de microestructures tridimensionals.

Mots clau: aplicacions d'ona quadrada, electrodeposició, nanopartícules metàl·liques, superfícies nanoestructurades

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1. INTRODUCTION

The preparation of low-dimensional structures of metals and semiconducting materials by electrodeposition on conducting surfaces provides a fundamental advantage of procedure simplicity, low cost, and reversibility of surface modification [1-3]. Electrodeposition, however, can be conducted by different strategies [4].

For more than two decades, Arvia and co-workers [5], Colb and co-workers [6] and Wieckowski and co-workers [7] demonstrated that surfaces can be microengineered by the application of symmetrical repetitive potential waveforms. Among the applied waveforms was the square wave potential regime. Repetitive cycles of the square wave may approximate a repetitive potential step experiment, thus rendering it advantageous in many useful applications [8]. For example, each cycle of the square wave comprises a forward and a reverse potential step, this repetitive potential stepping may lead surface atoms to dissolve and recrystallize on the surface, thus leading to a more favorable orientation. Now, in deposition of an element onto a given substrate, the rates of nucleation and particle growth of the deposited element structures are influenced by the experimental square wave parameters. Therefore, it would be possible to favorably manipulate these experimental parameters to yield preferential orientations of surfaces, or to control the size and shape of the deposited structures.

With the above premise in mind, and with the likelihood of a well-designed experimental control of the square wave parameters of frequency, lower and upper potential limits, and period of application, this work was undertaken to explore the possibility of forming nanostructures of tailored properties. The metals selected for the preparation of nanostructures comprise gold, silver and copper. These metals are known for their importance in electro-analysis, as well as electro-catalysis. As to the deposition substrate, tantalum was selected for being a member of refractory metals, and for its well-known, yet unique mechanical and anti-corrosion properties [9,10].

2. EXPERIMENTAL

2.1. Materials, Instruments, Cell and Electrodes

A potentiostat (273 A, Princeton Applied Research) interfaced to a computer through a GPIB interface along with an Echem® software was used for electronic control and data acquisition. A conventional H-shape electrochemical cell equipped with a multiple inlet system for admission of supporting electrolyte, and for purging and blanketing the solution with oxygen-free nitrogen was used. The reference electrode was an Ag/AgCl/ [Cl⁻] = 1.0 M, and all the potentials reported in this paper are referenced to this electrode. The working electrode was a 1.0 mm diameter tantalum electrode (99.99% pure, Goodfellow). The immersed part of the wire was curved in order to provide a mark for achieving a consistent surface area of the electrode.

All reagents used were highly pure certified analytical reagent (A.R.) chemicals, and were used as received from the suppliers without further purification. The auxiliary electrode was made of platinum (Johnson Matthey, 99.99% minimum purity). The purging nitrogen was G5 grade (99.999% minimum purity) supplied by the National Gas

Company and coupled with Oxisorb® cartridge (Supelco) to ensure effective removal of any traces of oxygen. All solutions were made from the above mentioned reagents dissolved in Millipore-Q water (Millipore) or triply distilled water, where the second distillation was carried out from basic potassium permanganate solution to get rid of any traces of organic impurities.

2.2 The deposition cell

A modified Polarographic 303A cell (Princeton Applied Research) was used for the electrodeposition of the metallic nanostructures. The cell was modified by bypassing the electronic circuitry of the 303 Polarographic Stand and using the three electrode cell system for the deposition process with Ag/AgCl, [Cl⁻] = 1.0 M reference electrode. Deposition of gold was carried out in 0.5 M H₂SO₄ + 1.0×10⁻³ M AuCl₄⁻ solution, while deposition of silver was achieved in 0.5 M H₂SO₄ + 1.0×10⁻³ M AgClO₄ solution. Copper deposition was conducted in 0.5 M H₂SO₄ + 1.0×10⁻³ M Cu(ClO₄)₂ solution. The solutions were stirred, purged and blanketed with oxygen-free nitrogen gas during the deposition period.

2.3 PROCEDURES

2.3.1 Pretreatment of tantalum substrates

At the beginning of each experiment, the tantalum electrode was chemically polished by immersion in a solution of 5:2:2 (v:v:v) 98% H₂SO₄, 65% HNO₃, and water followed by immersion in 48% HF and finally extensively rinsed with triply distilled water. The clean electrode was mounted in the electrochemical cell with the rest potential was determined (ca. -0.6 V). The electrode was cathodized at the rest potential for 5 min to reduce traces of oxide, if any, from the surface.

Figure 1 shows the voltammogram of tantalum produced under our experimental conditions. The voltammogram shows that the onset of surface oxidation is about -0.45 V. In all experiments the potential of the tantalum electrode was maintained below -0.6 V to avoid oxidation of the tantalum surface and to ensure that the metallic nanoparticles were developed on a clean, oxide-free tantalum surface.

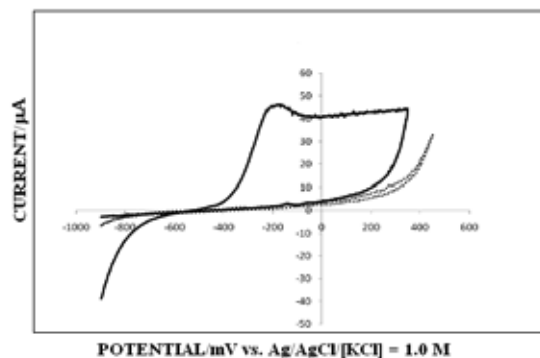


Figure 1: The voltammogram of polycrystalline tantalum electrode in 0.5 M H₂SO₄, dE/dt = 100 mV/s.

The square wave with the preset amplitude and frequency was generated by a function generator (Simpson, A240). The square wave was fed to the external input of the potentiostat. The desired lower and higher limits of the

potential regime were obtained by adjusting the applied electrode potential from the potentiostat and or the offset potential from the function generator. The square wave as applied to the electrode was screened by monitoring the applied potential through an oscilloscope (Telequipment S540). The frequency of the square wave was varied between 10 Hz and 1 kHz to explore the influence of frequency on the electrodeposited metallic structures. The duration of applying the square wave potential regime was also varied while the obtained structures were *in situ* investigated by voltammetry and viewed by SEM (Inspect™ F50, FEI). Voltammetric data proved very helpful in evaluation of the identity of the deposited particles and calculation of the relative surface coverage with the nanoparticles. The SEM micrographs were used for evaluation of the deposited structures in terms of size, shape, distribution and uniformity of the nanostructures at the surface of the tantalum substrate. EDX data were used to provide a supportive evidence for the identity of the deposited structures.

3. RESULTS AND DISCUSSION

Figure 1 shows the voltammogram of a clean tantalum electrode. Oxidation of the electrode surface commences nearly at - 0.45 V followed by a current peak at about - 0.2 V. After the oxidation peak on the positive going scan, the current levels off to a steady state value controlled by diffusion of the oxide ions into the tantalum lattice. Upon potential reversal, no cathodic counter peak is observed because of the stability of the formed tantalum oxide. On the second potential scan cycle, the overpotential for oxidation of tantalum surface is raised to a much higher potential because oxidation involves deeper layers of tantalum, a harder process that demands higher overpotential. In our experiments, the potential was maintained at values below - 0.45 V in order to ensure that the substrate for deposition is the unoxidized tantalum electrode.

Figure 2 shows three representative SEM micrographs of the electrodeposited nanostructures of gold, silver and copper on polycrystalline tantalum substrates. The identity of the nanostructures was confirmed by energy-dispersive x-ray spectroscopy (EDX) and voltammetry (Figure 3). The spectra unequivocally confirm the identity of the deposited nanostructures. Therefore, the SEM micrographs along with the EDX spectra prove the applicability of the square wave potential waveform approach for preparation of nanostructures.

The first observation that can be glimpsed from the SEM micrographs of gold on tantalum (Figure 2-A) is the apparent higher density of nanoparticles at the grain boundaries of tantalum surface. In fact this is not unexpected because of the higher surface free energy of grain boundaries. Though the nanostructures of the three metals were deposited at nearly similar conditions, there is a difference in the extent of surface coverage, the number of particles per unit area, in addition to differences in the shape and size of the particles. This indicates that certain physical properties of the developed particles are characteristic of the type of the deposited metal, which might be attributed mainly to the characteristically inherent differences in the standard electrode potential of these metals. Consequently, the rates of deposition of different

metals will vary with variation in the overpotential applied to each of these three metals from the other two.

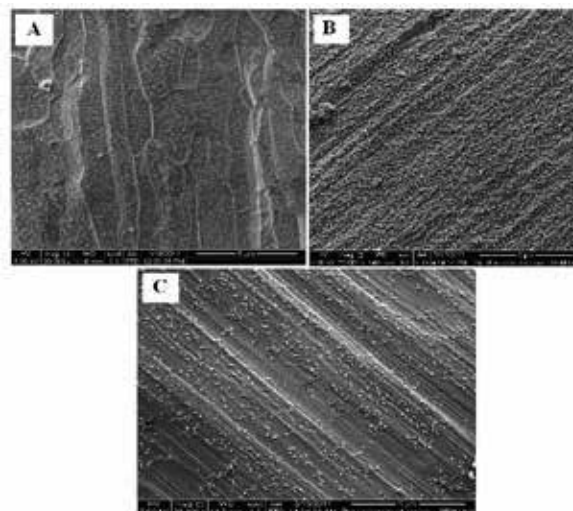


Figure 2: SEM micrographs of deposited nanostructures of (A) gold, (B) silver, and (C) copper on a clean polycrystalline tantalum substrate. Experimental parameters: $E_i = - 0.3$, $E_h = + 0.1$ V, for deposition of gold, $E_i = - 0.3$ V, $E_h = 0.00$ for silver, and $E_i = - 0.5$ V, $E_h = - 0.1$ V for copper. Deposition time = 60 s, square wave frequency = 100 Hz, gold, silver and copper were deposited from 10^{-3} M $AuCl_4^-$, 10^{-3} M Ag^+ and 10^{-3} M Cu^{2+} dissolved in 0.5 M H_2SO_4 respectively. Square wave amplitude = 0.4 centered at - 0.4 V.

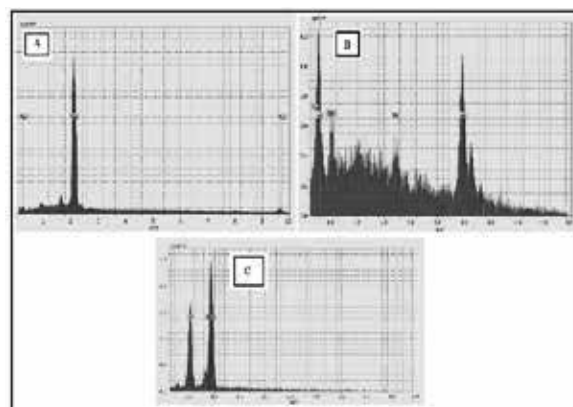


Figure 3: Energy-dispersive x-ray spectra for electrodeposited nanostructures of (A) gold, (B) silver, and (C) copper.

Figure 4 shows the cyclic voltammograms for gold, silver and copper nanostructures deposited on tantalum substrates. The voltammetric features of these voltammograms are very similar to the respective, yet well-known characteristic voltammetric features of gold, silver and copper electrodes. This observation reconfirms the identity of the deposited particles, which was evident from the EDX data. The charge underneath the oxygen desorption peak (Figure 4-A) was taken as a quantitative measure of the total surface area of the deposited gold on tantalum surface, or of the coverage of the tantalum surface with gold nanoparticles. Similarly the charge underneath oxygen desorption from silver surface was used as an index for the total surface area of silver nanoparticles, or

the surface coverage with silver nanoparticles. For copper, peak 3 in Figure 4-C, the charge under the most prominent surface oxidation peak was taken as an index of the total surface of copper deposited nanoparticles, or the surface coverage with copper nanoparticles. In our subsequent discussions the relative coverage is based on this type of calculations.

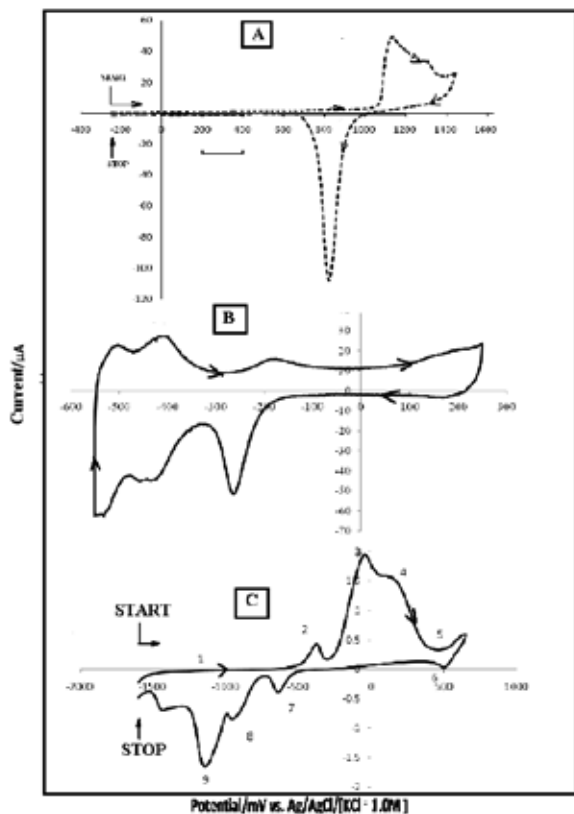


Figure 4: Cyclic voltammograms of nanostructured electrodes of (A) gold, (B) silver, and (C) copper deposited on tantalum substrate. Gold and silver were recorded in $0.5\text{ M H}_2\text{SO}_4$, while copper was recorded in 1.0 M KOH solution. $dE/dt = 100\text{ V/s}$.

The size, shape, and uniformity of distribution of the nanoparticles of the three metals were found to depend on the frequency, amplitude and time of application of the square wave. The concentration of the metal ion in the supporting electrolyte was also found to play a critical role in the characteristics of the grown particles. These effects will be discussed in more detail in the following sections.

3.1 The effect of the square wave frequency

The charge underneath oxygen desorption peak was estimated from the corresponding voltammogram for every prepared gold nanostructured electrode that was obtained at a particular square wave frequency. Figure 5 shows a plot of those charge estimates against the corresponding frequencies of the square wave applied for producing the gold nanostructures, and the curve shows a maximum at 100 Hz. An investigation of the SEM micrographs of the produced nanostructures shows that the largest number of particles was produced at a 100 Hz frequency, too (Figure 6). The same observation was also apparent for both of silver and copper, where 100 Hz was the optimal frequency for growth of the nanoparticles.

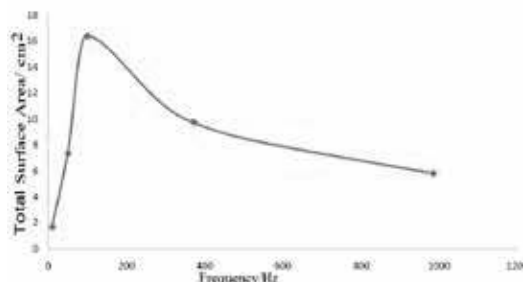


Figure 5: A plot of gold total surface area calculated from cyclic voltammograms of deposited gold particles as a function of the frequency of the applied square wave. Experimental parameters: $E_i = -0.3$, $E_h = +0.1$ V, $[\text{AuCl}_4^-] = 1.0 \times 10^{-3}\text{ M}$, deposition time = 60 s.

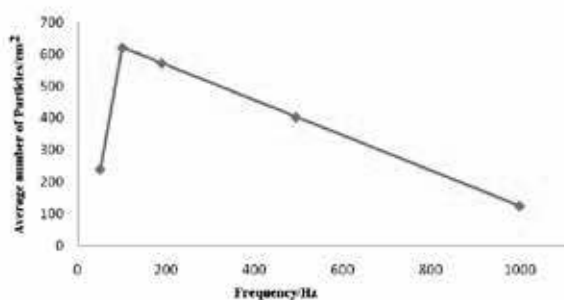


Figure 6: A plot of the number of gold nanoparticles/cm² estimated from the SEM micrographs as a function of the frequency of the applied square wave potential regime.

The larger number of nanoparticles grown at 100 Hz frequency dictates larger total surface and consequently larger charge underneath the oxidation peak, and hence a larger charge for oxygen desorption from the surface. An intermediate frequency is expected to produce greater number of nanoparticles, since this presents a balance between the number of pulses per unit time, and the time spent at the lower potential that is necessary for deposition. At high frequencies, the time scale for the (HI) and (LO) values of the square wave becomes relatively short, which coupled with an ohmic potential drop, the charging current will render the application of the square wave useless. On the other hand, at very low frequencies, the number of pulses to the deposition potential becomes very low, while the time of deposition per potential cycle is relatively very long. This affects the balance between particle growth and nucleation mechanisms, in which case an optimal intermediate frequency becomes more adequate. Moreover, it was also observed that the frequency applied to the square wave does affect the uniformity of the distribution of the particles, the size and shape of the grown particles, for each of the three metals investigated.

3.2 The Effect of metal concentration and deposition time

For electrodeposition of nanostructures of each of the three investigated metals, it was found that an increase in the time of deposition monotonically leads to larger deposited particles. Moreover, nanostructures were observed to grow at 10^{-4} M and 10^{-3} M concentrations, especially when combined with shorter deposition times. Furthermore,

larger concentrations and/or longer deposition times lead to the formation of 3-dimensional structures (Figure 7). These results can be explained on basis of two competing mechanisms for deposition of the metal on tantalum substrate, namely nucleation and particle growth [11]. The results of this work strongly suggest that particle growth is the prevailing mechanism of metal deposition at high concentrations and long deposition times. The initial stages of deposition involve nucleation, which occurs selectively at high-energy surface sites. These high-energy surface sites may include surface defects, voids, adatoms, or grain boundaries. At low ion concentration, nucleation prevails because of the availability of high-energy surface sites. On the other hand, at high concentration of depositing ions, high surface energy sites are relatively limited thus making particle growth mechanism prevalent. On the same basis, the effect of deposition time can be explained. At short deposition times, nucleation mechanism prevails because of the availability of high-energy surface sites, while particle growth prevails when most of these sites are consumed at long deposition times. This would necessarily enhance the formation of 3-dimensional structures, at long deposition times.

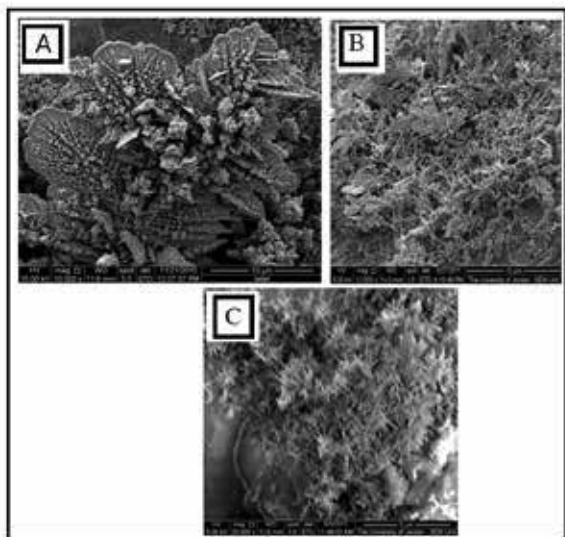


Figure 7: SEM micrographs for (A) gold microstructures deposited from 1.0×10^{-2} M AuCl_4^- solution, (B) silver microstructures deposited from 1.0×10^{-2} M Ag^+ solution, and (C) copper microstructures deposited from 1.0×10^{-2} M Cu^{2+} solution. Experimental square wave parameters: $E_l = -0.3$, $E_h = +0.1$ V centered at -0.1 V, amplitude = 0.4 V, frequency = 100 Hz, and deposition time = 300 s.

3.3 The effect of square wave amplitude and the position of the center of the square wave along the potential axis.

The effect of the amplitude of the square wave is exemplified in Figure 8. Figure 8 shows two voltammograms for gold nanoparticles obtained at two amplitudes; 0.4 V and 1.0 V where both square waves were centered at -0.6 V.

From the voltammograms, it is very apparent that the charge underneath the oxygen desorption peak is much larger at a larger amplitude of the square wave. This observation, can easily be explained on the basis that larger amplitude means that the deposition occurs at

lower potential (-1.1 V) while upon application of a 0.4 V amplitude square wave, the deposition occurs at -0.8 V. The lower limit of the square wave, that is the potential at which the electrodeposition occurs, is associated with a more facile kinetics of deposition that leads to higher surface coverage of the deposited particles.

The position of the center of the square wave is expected to impose a critical influence on the feasibility of the deposition process. For example, at a lower position of the center of the square wave, the deposition process occurs at a higher rate where more particles are formed on the surface. In contrast, at a relatively higher position of the center of the square wave (i.e., at more positive potentials), the rate of deposition decreases where the deposition process becomes less spontaneous. Generally speaking, the shift towards more positive potentials may lead to the formation of metallic oxide particles, a topic that shall be addressed in a separate paper.

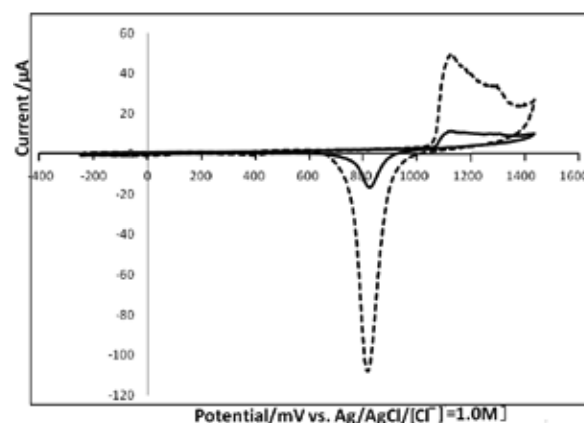


Figure 8: Cyclic voltammogram for a gold nanostructured electrode on a tantalum substrate produced at (----) 1.0 V amplitude and (—) 0.4 V amplitude. Experimental parameters: deposition time = 120 s, frequency of the square wave = 100 Hz, gold concentration = 1.0×10^{-3} M, scan rate = 100 mV/s.

4. CONCLUSIONS

In the present work, the notion of using a simple square wave potential regime for the preparation of gold, silver and copper nanostructured electrodes was verified. The square wave parameters of frequency, amplitude, and the position of the center of the square wave along the potential axis were found to exert significant influence on the properties of the deposited structures. Moreover, the concentration of the ion of the deposited metal, and the duration with which the square wave is applied to the electrode, also influence the properties of the deposited structures. For example, it was found that higher ion concentrations and/or longer deposition times lead to the formation of microstructures at the electrode surface.

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