

Full Paper

Platinum Nanoparticle Electrode Modified Iodine using Cyclic Voltammetry and Chronoamperometry for Determination of Ascorbic Acid

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Abstract- This study investigated the oxidation of ascorbic acid (Vitamin C) using a platinum nanoparticle electrode coated with an iodine monolayer, called a modified electrode. The electrode were grown using the cyclic voltammetry technique and the electrochemical measurements were taken using the cyclic voltammetry and chronoamperometric technique. In the case of platinum nanoparticle electrode modified iodine by and ascorbic acid, the analyzed the anodic peak current and anodic maximum potential is done. The also examined the effect of the concentration of ascorbic acid and the effect of the scan rate on anodic top parameters. The results show that the anodic current peak increases and that the anodic peak potentials increase in comparison to the clean electrode to a negative value. Anodic peak current increases with scan rate of ascorbic acid increases. As the ascorbic acid concentration and scan rate increase, the anodic peak potential changes to more positive values. The SEM and EDX demonstrate some fascinating characteristics of the uniform particle distribution, growth and self-assembly of the iodine-modified platinum nanoparticle. The sensor was ascorbic acid with a sensitivity of $0.215 \mu\text{A}/\mu\text{M}\cdot\text{cm}^2$ and a detection limit of $0.01 \mu\text{M}$ ($R^2=0.994$). The results show that the iodine-modified platinum nanoparticle electrode developed can be used in food sampling to voltammetric determine Vitamin C.

Keywords- Modification electrodes; Ascorbic acid; Cyclic voltammetry; Platinum; Nanostructured electrode; Nanoparticles

1. INTRODUCTION

Ascorbic acid (H₂A) is a nutritive in many foods, including citrus fruit and leafy vegetables, commonly known as vitamin C. In avoiding diseases like scurvy, it plays an important role; it scavenges free radicals. In food processing, pharmaceutical and medicinal applications, H₂A is commonly used as an antioxidant. Fast, delicate H₂A concentration detection in real time is very interesting [1-3]. Several analytical methods for determining H₂A have been established, chemiluminescence [4], enzymatic methods [5, 6], titrimetry [7], spectrophotometry [8,9] and electrochemical [10-12]. Due to quick analysis, lower concentrations and simplicity of activity, electrochemical measurements of ascorbic acid are gaining interest [13-15]. H₂A was amply tested for amperometric determination in aqueous solutions. High potential oxidation in H₂A can affect practical applications; CMEs are designed to reduce overpotential in certain chemically modified electrodes. There has been recorded a potential of 0.6 V versus SCE to directly oxidize H₂A in a bare Pt electrode [14].

Table 1. gives a short summary of the work on ascorbic acid determination

System	Technique	Sensitivity ($\mu\text{A}/\mu\text{M}\cdot\text{cm}^2$)	Detection Limit (μM)	References
3D graphene foams-CuO-GCE	CV	2.06	0.43	[16]
AgNPs-RGO-GCE	CV	1.64	10	[17]
ERGO-GCE	DPV	0.171	0.5	[18]
CTAB-GO-MWNT-GCE	DPV	401.64	1	[19]
Solar graphene-GCE	CV	0.00049	-	[20]
MWCNT-GCE	SWV	0.471	1.4	[21]

An electrode-modified biosensor with an independent monolayer has a detection limit of 1.4 nM for ascorbic acid [22]. Both the aminated glass carbon electrode and the gold electrode have been covered in oxygen driven hydrophobic ascorbate oxide membranes for detection the amperometric ascorbic acid, which are based on consumption of oxygen. These biosensors are responsive and have a fast response time in just 1 minute [23]. Recently developed methods for voltammetrically defining the molecular low weight (i.e. ascorbic acid) and drugs, are fast, simple, selective and sensitive without time-consuming separation [24]. For the measurement of electrocatalytic ascorbic acid in a carbon electrode, adjusted with ferrocenylethynyl, cyclic and differential pulse voltammetry were used [25]. In measuring the amount of ascorbic acid in citrus juices and soft drinks cyclic voltammetry was

applied to the bare Pt electrode [26]. For electrochemical oxidation and selective determination of ascorbic acid, cyclic, linear and square-wave voltammetry in pharmaceutical formulations has been investigated [27]. The range for linear responds to DPV was 3.52-176.1 $\mu\text{g ml}^{-1}$, and SWV was 0.88 $\mu\text{g ml}^{-1}$. In cyclical voltammeter studies on Pt electrodes, the growth of Pt surface oxide and the anodic response of various interfering materials (glucose, cystine and oxalate) have been strongly influenced by the application of fluorosurfactant Pt electrodes [28]. Voltammetry is an increasingly popular tool for ascorbic acid determination in real specimens because, even if compared with more expensive technique, it provides low detection rates [29]. In addition, a voltammetric biosensor built into an automated SIA device has also been used to simultaneously detect vitamin C and glucose [30]. Recent combinations of various voltammetry techniques with modified ascorbic acid sensors have been made; ascorbic acidification based on its oxidation at a fluoren modified carbon electrode was calculated using square-wave voltammetry and the procedure for the determination of the ascorbic acidification of citrus juice has been applied [31]. Interesting work was found in the new era in the design and development of nanoparticular sensors [32]. In particular, the highly interesting structure of the surface, good electrical and mechanical characteristics, solid stability and a low aggregation have been found to be the perfect supporting materials for the electrocatalytic [33]. Such properties clearly support their use for commercially viable applications as catalysts. For example, nanoparticles of gold and platinum possess their own mechanical strength and electric properties. Platinum nanoparticles have different electrode changing characteristics [34]. The aims of this research are to study the characteristics of H₂A electrical oxidation on Pt nanoparticle electrodes and modified iodine electrodes with low potential applied. The electrochemical competencies of these electrodes in the presence and absence of H₂A have been analysed with cyclic voltammetry and chronoamperometry.

2. EXPERIMENTAL

2.1. Reagents

Sulfric acid (97%, Fluka, Germany), ascorbic acid (99.7%, Anala R, England), Iodine crystals: (99%, GALNLAND CHEMICAL COMPANY, UK). Both solutions were formulated using double distilled deionized water. The National Gas Company supplied purging nitrogen to remove traces of oxygen in conjunction with Oxisorb® cartridge (Suplico).

2.2. Apparatus

The use of potentiostat (A273, USA) was used for electrochemical measurements such as cyclic voltammetry (CV). A conventional three-electrode cell, Platinum nanoparticle electrode working electrode on tantalum substrate is concentrated at the 1×10^{-4} M

concentration by the square wave potential applications in conditions; 0.4V amplitude, the square wave with -0.4 to 0.0 V Hi and Lo values and the deposition time was 120s [35].

The Ag/AgCl [KCl 1.0 M] reference electrode was used at room temperature as an electrode reference and an auxiliary electrode made of 0.2 mm platinum wire, Aldrich chem.co (99.99%, USA). The SEM Scanning electron microscope (Inspect F50, FEI Company, Eindhoven, Netherlands) was investigating the surface morphological characterization of the electrode. The SEM was combined with electron EDX microanalysis, which enabled an examination of the basic composition of the deposited structures.

2.3. Sensing procedure

The applied potential was defined in the presence and absence of H₂A by polarization curves. The mass transfer of H₂A to the electrode surface was possible through any potential applied within the appropriate range. First, the relevant range was defined and, once the background current and the amperometric response (sensing) current for the operating electrode were stable, a measured volume of H₂A was injected into the flask.

3. RESULTS AND DISCUSSION

3.1. Characterization of Pt nanoparticle electrode modified by iodine

The synthesized Pt nanoparticle electrode modified by iodine was characterized for functional groups using (SEM, scanning electron microscopy), (CV, cyclic voltammetry) and (EDX, energy-dispersive X-ray spectroscopy).

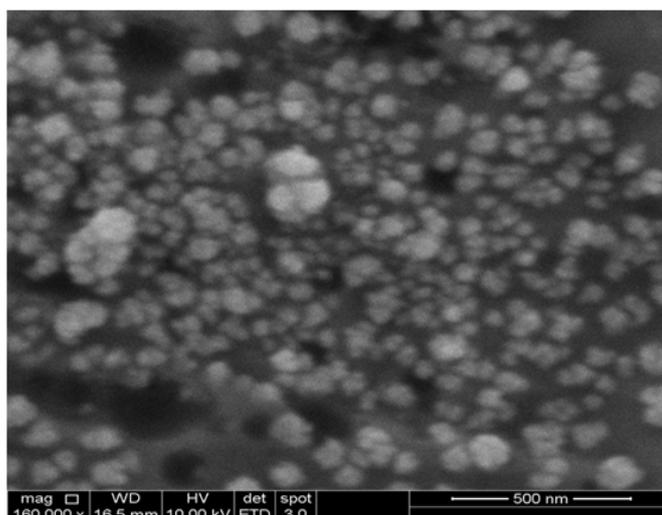


Fig. 1. The SEM micrographs of Pt nanoparticle electrode modified by iodine

Fig. 1 shows the typical SEM image obtained for the electrodeposited Pt nanoparticle electrode modified by iodine. Herein the SEM image has been obtained for 500nm surface

areas. The SEM image shows that the Pt nanoparticles are uniformly dispersed on the electrode surface. The identity of the Pt nanoparticle electrode modified by iodine is further confirmed by the EDX spectrum of the deposited particles (Fig. 2).

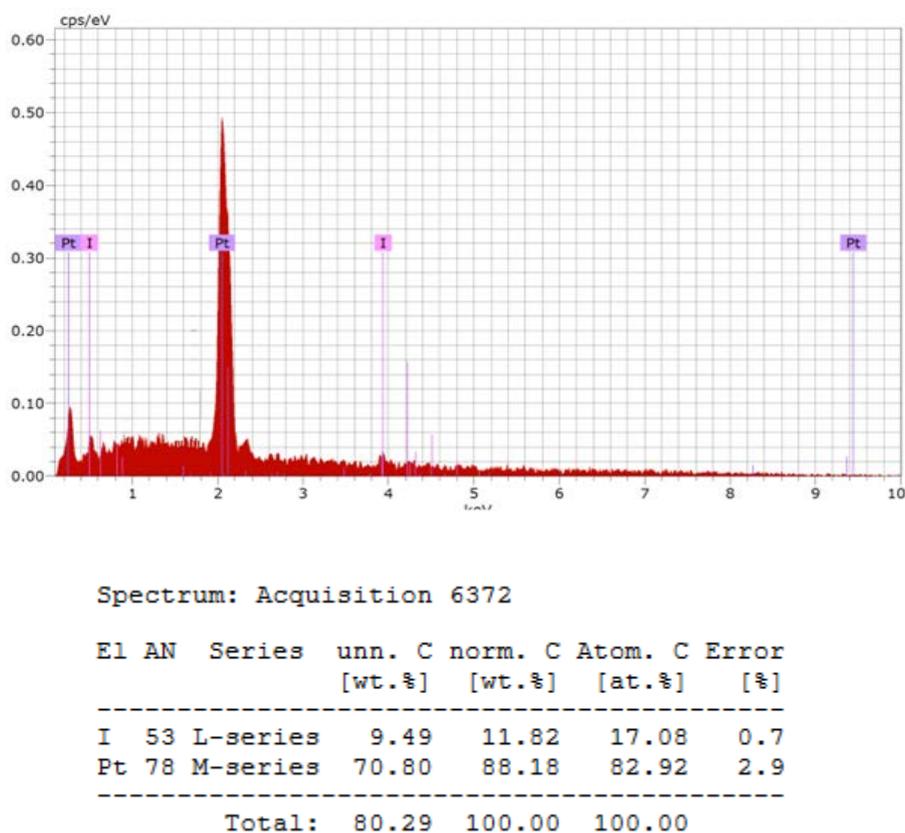


Fig. 2. EDX spectrum of Pt nanoparticle electrode modified by iodine

The electrochemical behaviour of Pt nanoparticle electrode modified by iodine was studied using cyclic voltammetry at a scan rate of 100 mV/s. The Fig. 3 shows the iodine coated platinum nanoparticles electrode representative voltammograms recorded in 0.5 M H₂SO₄ (dashed line) superposed to the process voltammograms of the bare platinum electrode nanoparticles (solid line). The absence of redox (oxidation/reduction) activity and in particular oxygen and hydrogen adsorption indicates a near total surface suppression between the hydrogen production limits (around -0.2 V) and surface iodine suppression levels (around 0.95 V). The iodine is partially desorbed when the potential of the electrode with iodine-coated scans is above 0.95 V. The restoration, between its hydrogen and the oxygen production limits, of cleanness in the surface that involves the daily washing of the work electrode and the compartment requires a number of possible cycles. A 1.18 V based peak displays a platinum nanoparticle electrode with iodine electrooxidation. Nevertheless, the iodine is stable if the potential electrode does not exceed 0.95 V. Therefore, the practical analytical potential range usually varies from -0.1 to 0.95 V.

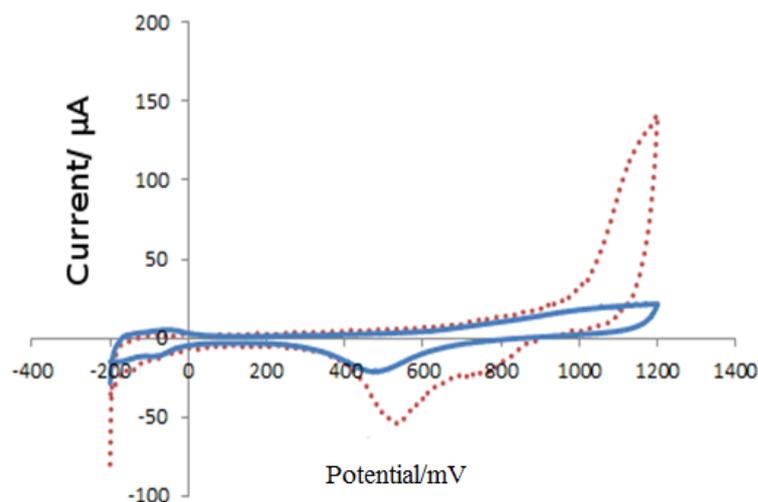


Fig. 3. Voltammograms of platinum nanoparticle electrode (solid line) and iodine-coated platinum nanoparticle electrode (dashed line). At a scanning rate of 100 mV/s both voltammograms were registered in 0.5 M H_2SO_4 .

H_2A oxidation on the nanoparticle platinum electrode in the acid solutions. Fig. 4 shows cyclic voltammograms in 0.5 M H_2SO_4 and containing 0.01 M H_2A : curve 1 (blue) is the cycling performed with the clean electrode; curve 2 (red) was obtained in the nanoparticle platinum electrode modified by iodine monolayer.

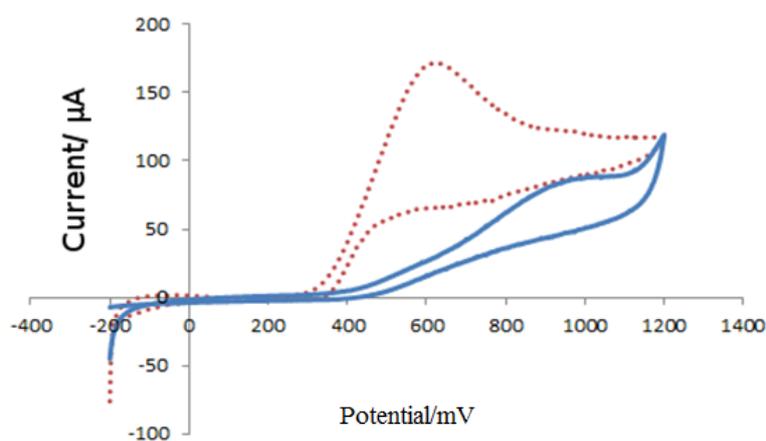


Fig. 4. Voltammograms of platinum nanoparticle electrode (solid line) and iodine-coated platinum nanoparticle electrode (dashed line) in the presence of 0.01 M H_2A scanned at 100 mV/s in 0.5 M H_2SO_4 solutions.

It can be seen that, for the clean electrode in the solution of ascorbic acid (curve 1), a high anodic peak of current appears around 0.58 V, which, according to the literature, corresponds to the oxidation of ascorbic acid at a clean nanoparticle platinum electrode versus a reference

Ag/AgCl electrode. In the potential sweeping of the nanoparticle platinum electrode modified by iodine monolayer curve 2, corresponds to the electrode with the iodine monolayer in the presence of ascorbic acid. As can be observed, the anodic current peak increases and shifts to more negative potentials. This means that the electrode modified by iodine monolayer presents electro-catalytic activity to ascorbic acid. The increase of current peak indicates that a higher amount of species was oxidized, while the shift in potential shows higher facility in oxidizing these species. This shift of the potential to lower values is interesting, as it increases electrode selectivity. When the reverse scan is done, the formation of Pt oxides is inhibited by H₂A oxidation. Since no other reduction peaks have been found, it can be concluded that platinum electrode H₂A oxidation reactions are irreversible in acid solutions [36]. For alkaline solutions, a reverse analysis of the platinum nanoparticles showed no peak reduction. The H₂A oxidation reaction was therefore irreversible. To detect H₂A in the platinum electrode nanoparticles with low overpotential.

The voltammograms further indicate that the Pt nanoparticle electrode modified by iodine showed higher currents for H₂A oxidation compared to bare Pt nanoparticle electrode. The increased peak currents are largely the result of increased electroactive surface area of the Pt nanoparticle electrode modified by iodine. Both bare Pt nanoparticle electrode and Pt nanoparticle electrode modified by iodine-oxidized ascorbic acid.

3.2. Effects of ascorbic acid concentration

The sensing mechanism includes the adsorption onto the iodine-modified Pt surface of the ascorbic acid molecules in the solution. The molecules for ascorbic acid are hydrolyzed with water and dehydroascorbic acid oxidized [37]. This process of H₂A oxidation can release the equivalent electrons and current that can be detected. In Fig. 5, ascorbic acid oxidation has been shown to be an irreversible process due to the absence of a reduction peak.

The voltammograms derivable from the ascorbic acid concentration variability are shown in Fig. 5. As can be seen, as the concentration increases, the peak current increases significantly and the peak potential moves towards more values that are positive. The current increase indicates that the modified electrode in the presence of ascorbic acid is well tolerant and stable. On the other hand, the change in ascorbic acid oxidation's peak potential value can, be explained by an increase of ascorbic acid molecules on the electrical surfaces.

The number of molecules on the electrode surface will also increase at greater concentrations of ascorbic acid. The concentration of such molecules in the electrodes falls as a result of oxidation, which is that a large species flow is produced from the centre of the solution to its surface to maintain a surface concentration. The behaviour of the ascorbic acid concentration with anodic peak current is shown in Fig. 5-A.

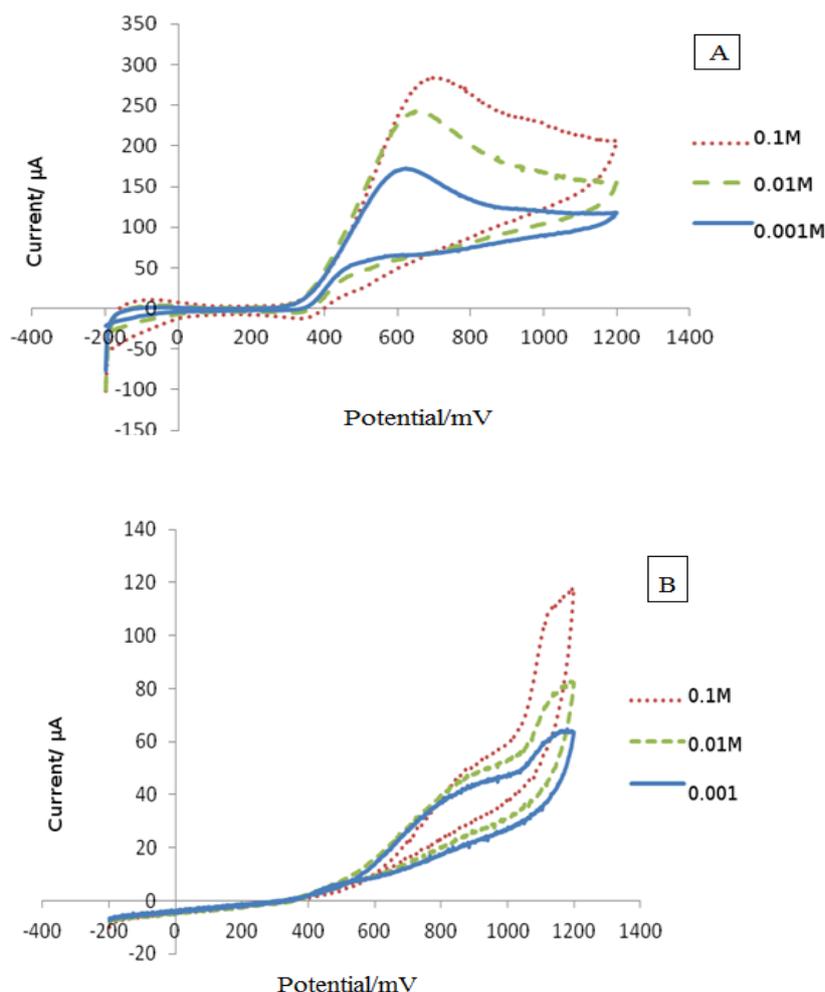


Fig. 5. A: Voltammograms of platinum nanoparticle electrode, B: Voltammograms of iodine-coated platinum nanoparticle electrode, varying the concentration ascorbic acid of 0.1, 0.01 and 0.001M H₂A, scanned at 100 mV/s in 0.5 M H₂SO₄ solutions.

As can be observed, the increase is practically linear—a curve with a correlation coefficient of 0.994. This data confirms that within the concentration range in study the electrode shows good stability. The limit of detection has not yet been analysed, but we know it is below the minimum figure presented here. Fig 5-B shows the variation of the peak potential with concentration. It can be observed that the shift of the potential to more positive values also has a linear behaviour with the increase of the ascorbic acid concentration. This may be because the results may also be interfering with other unwanted species, which can be oxidized to high potential. Thus, this data indicate that the modified electrode in study has good selectivity, because the smaller oxidation potential is found at the lower concentration. Its limit of detection will probably be even more negative in potential. The maximum oxidation peak current achieved was directly commensurate with the ascorbic acid concentration. The calibration diagram was drawn with the linear regression equation of

$R^2=0.994$ against concentrations of ascorbic acid, with the sensitivity of $0.215\mu\text{A}/\mu\text{M}\cdot\text{cm}^2$ (Fig. 6).

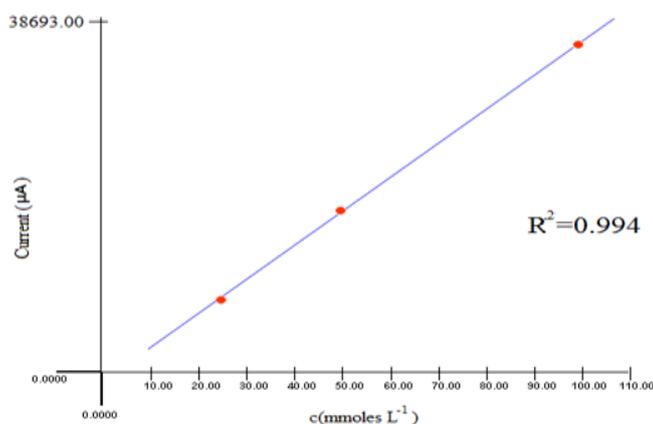


Fig. 6. Calibration graph for the determination of ascorbic acid by cyclic voltammetry within of 0.1, 0.01 and 0.001M H_2A

3.3. Effect of scan rate

The effect of scan rate on oxidation and reduction currents on Pt nanoparticle electrode modified by iodine was investigated by cyclic voltammetry in 0.5 M H_2SO_4 and 0.1 M H_2A solutions at different scan rates (25-100mV/s) in the potential range -0.2 to 1.2 V (Figure 7). It can be observed that the current anodic peak increases as the scan rate increases, and it shifts to the right, that is, to a region of more positive potential. The values of current peak and the peak potential were taken from the voltammograms, traced as a function of the scan rate, and are represented in Fig 7. As can be observed, the current of anodic peak increases linearly with the scan rate, and there is a change in inclination at 100 mV/s.

The linear increase of the anodic peak current with the increase of the scan rate indicates that the transference of charge between the species within the iodine monolayer coating Pt nanoparticle takes place more rapidly, and the change of inclination in the curve above 100mV/s means that the mechanism of the redox process is different for high scan rates. Proposed a mathematical model that shows that the anodic peak current is proportional to the concentration of electro-active species on the surface of the electrode [37]. Investigated the effect of scan rate on the parameters of the peaks of the voltammograms obtained from the oxidation of ascorbic acid using a modified electrode. The linear rise of the anodic current is commensurate with the square root of the scanning rate and the concentration in the solution of the electroactive species [38]. The shift of the potential to more positive has a more exponential behaviour, i.e., the values tend to maximum. This indicates that there is a

limitation to the diffusion process, that is, at very high scan rates the concentration of ascorbic acid on the surface of the electrode does not vary.

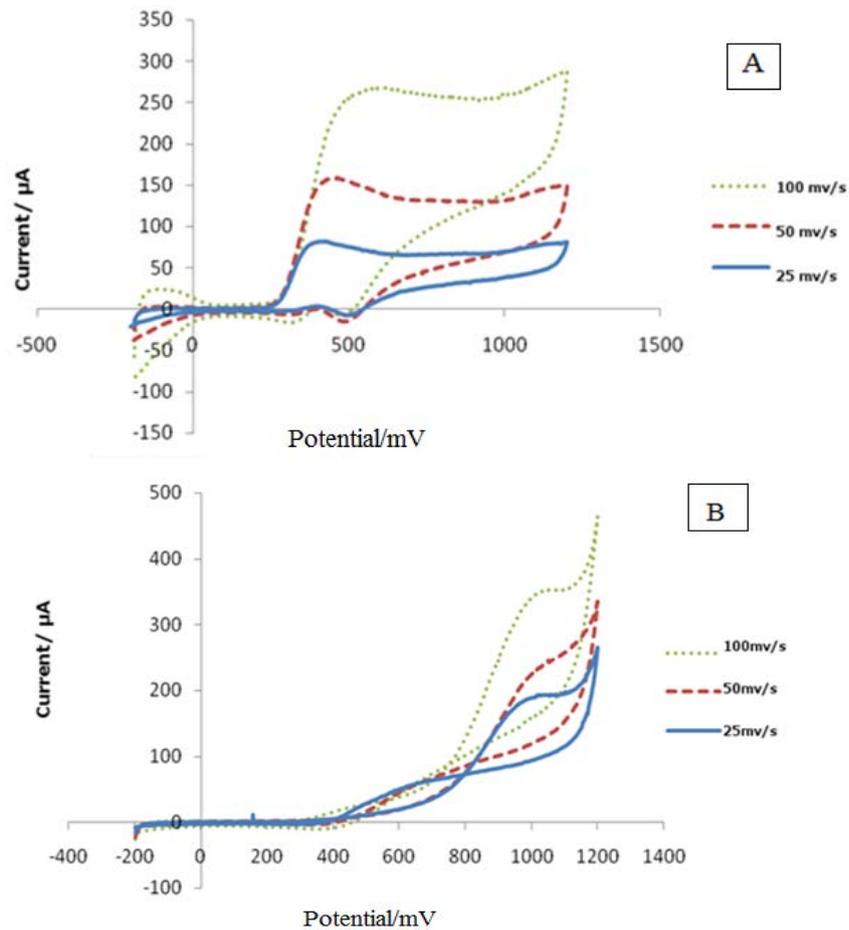


Fig. 7. A: Voltammograms of platinum nanoparticle electrode, B: Voltammograms of iodine-coated platinum nanoparticle electrode, varying the scan rate of 25, 50 and 100 mV/s in 0.5 M H₂SO₄ and 0.1 M H₂A solutions

3.4. Morphological characterization

Chronoamperometric technology is the efficient of ascorbic acid in the evaluation, on the Pt nanoparticle electrode modified by iodine in the 0.5 mM H₂A, of the electrocatalytic activity and current density–time responses for of ascorbic acid oxidation at its fixed potential from 0.4 up to 0.8 V in Fig. 8 of iodine-modified PtNPs. The forward reaction for oxidation of ascorbic acid was calculated according to the equation 1:

$$K_f = I_k/nFAC^* \quad (1)$$

where (A: the surface area, K_f: the kinetic reaction forward, n: transmitted electrode no., C*: ascorbic acid concentration and F: constant Faraday). The Pt nanoparticle electrode modified

iodine shows the highest current density (53 mA cm^{-2}), while in 0.3 seconds the Pt nanoparticle electrode shows a present density of 17 mA cm^{-2} . These data show increased operation and iodine stability. The modification of metal, which can enhance catalytic effectiveness and the bifunctional mechanism or structure of the ligand, can also explain these findings.

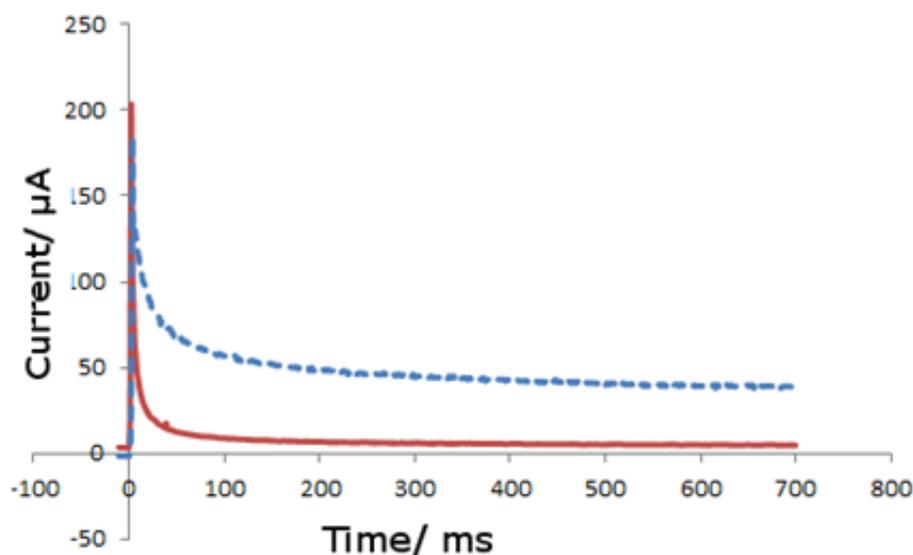


Fig. 8. Current vs. time as potential kept at 0.4 to 0.8 V in 0.5 M H_2SO_4 + 0.01 M H_2A on of iodine-coated platinum nanoparticle electrode (dashed line), and platinum nanoparticle electrode.

4. CONCLUSION

According to the results, we can conclude that the nanoparticle platinum electrode containing the iodine monolayer, modified electrode, presents electrocatalytic activity and good selectivity for ascorbic acid. This electrode can therefore be improved and used as a sensor for the identification of ascorbic acid in natural systems. Pt nanoparticle electrode, modified by iodine, showed better electrocatalytic activity against ascorbic acid oxidation and was able to reactive ascorbic acid over a broad range of well stable concentrations with good sensitivity ($0.215 \text{ } \mu\text{A}/\mu\text{M}\text{-cm}^2$).

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