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Electrocatalytic oxidation of vitamin C using an aluminium electrode modified by copper oxide

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ABSTRACT

Effect of Cu_2O nanoparticles on aluminium electrode by electrodeposition method, which is utilized to determine the ascorbic acid (AA) by voltammetric method. Well-defined oxidation peak potential of Cu_2O that appears in phosphate buffer medium electrocatalyzed and improved dramatically the oxidation signal of ascorbic acid. Optimization parameters such as, pH, effect of Cu_2O nanoparticles, scan rate and electroactive interference were evaluated. A linear calibration graph was obtained over the ascorbic acid with a concentration range of 5 x 10^{-6} mol/L to 110 x 10^{-6} mol/L. The detection limit (DL) of ascorbic acid was estimated as 0.5 µM. A big advantage of aluminium electrode material wae the ease of modification and acheived higher selectivity, to low the overpotential, better limits of detection and a wider range of linear response toward the analyte.

Keywords: Electrochemical sensor, Cu_2O nanoparticles, Aluminium electrode, cyclic voltammetry, Vitamin C.

1. INTRODUCTION

Vitamin C can be originate in any biological systems and foodstuffs, namely fresh vegetables and fruits, as the most biquitous water-soluble vitamin ever discovered. Rich sources include blackcurrant, citrus fruit, leafy vegetables, tomatoes, green and red peppers, etc. Vitamin C is involved iron absorption, collagen synthesis and immune response activation and participates in wound healing and osteogenesis, helps maintaining capillaries, bones, and teeth.

Ascorbic acid excess can lead to gastric irritation and one of its metabolites, oxalic acid, causes renal problems [1]. In some cases, excessive quantities of ascorbic acid may result in the inhibition of natural processes occurring in food and can contribute to taste/aroma deterioration; [2]. Another drawback of ascorbic acid excess is its ability to act as a strong antioxidant only in aqueous media and in the absence of heavy metal cations. In the presence of heavy metal cations, it can even act as a prooxidant: ascorbate ion is an excellent reducing agent that can reduce ferric (Fe^{3+}) to ferrous (Fe^{2+}) iron, while being oxidized to dehydroascorbate [3, 4].

Studies of nanobiosensors based on semiconductor nanostructured metal oxides are of practical and theoretical importance in biological science, environmental science and analytical chemistry. These one-dimensional nanostructured metal oxides have profound applications in optics, optoelectronics, sensors, and actuators duo to their semiconducting, piezoelectric, and pyroelectric properties. Nanostructured metal oxides not only possesses high surface area, nontoxicity, good biocompatibility and chemical stability, but also shows fast electron communication features made the materials to be able to function as biomimetic membrane material to fix and modify proteins.

Among the various types of nanomaterials that have been developed, nanostructured metal oxides (NMOs) have recently aroused much interest as immobilizing matrices for biosensor development [5-7]. Nanostructured oxides of metals such as zinc, iron, cerium, tin, zirconium, titanium, metal and magnesium have been found to exhibit interesting nano morphological, functional biocompatible, non-toxic and catalytic properties. These materials also exhibit enhanced electron-transfer

kinetics and strong adsorption capability, providing suitable microenvironments for the immobilization of biomolecules and resulting in enhanced electron transfer and improved biosensing characteristics.

Among various metal oxides, the CuO has been studied as a unique and attractive monoxide material due to its both fundamental investigations and practical applications [8,9]. CuO is a p-type metal oxide semiconductor with narrow band-gap (1.2 eV) and exhibiting versatile range of applications. It has been effectively used in the fabrication of electrical, optical and photovoltaic devices, heterogeneous catalysis, magnetic storage media, gas sensing, field-emission (FE) emitters, lithium ion electrode materials, and so forth [10]. Even though having versatile properties with various applications but the amperometric biosensor applications of CuO nanostructures are rare [11-13]. The previously reported works on CuO based glucose biosensors exhibited lower sensitivity and higher detection limits, hence more works are needed to fabricate high-sensitive with low detection limit CuO nanostructures based glucose biosensors.

In the present study, we fabricated a metal oxide made of Cu_2O nanoparticles modified aluminium electrode by electrochemical deposition. The modified electrode was characterized by XRD, EIS and cyclic voltammetry (Cv). The outcomes presented here are more evident that Cu_2O/Al modified electrode could bring new capabilities for the electrochemical devices by combining the advantages of Cu_2O nanoparticles, and can be readily used for determination of the ascorbic acid in various fruit samples.

2. EXPERIMENTAL

2.1. Chemicals

Ascorbic acid was obtained from Sigma Aldrich (USA). Copper Sulphate, acetone, sodium hydroxide, sodium dihydrogen phosphate, potassium ferrocynaide, nitric acid and sulphuric acid were analytical grade chemicals which were obtained from E-MERCK and all chemicals were used as such without any further purification. Doubly distilled deionized water was used throughout the work. Stock solution of AA (1.0×10^{-2} M) were prepared daily in deoxygenated distilled water and stored in a dark and cool place. This solution was diluted to the appropriate concentration, and its pH was adjusted by addition of acetic acid.

The phosphate buffer (PBS) solution was made up from NaH_2PO_4 and adjusted to pH 7.2 by NaOH. The supporting electrolytes of other pH were prepared by adding suitable quantities of acid or alkali and checking the pH of the medium using Elico pH meter.

2.2. Instrumentation

The electrochemical analyzer from CHI instruments Model 760 was employed for various electrochemical studies performed. This instrument uses the latest analog and microcomputer design to provide high performance, better precision and greater versatility in electrochemical measurements. This instrument was employed for performing voltammetric studies. The nanostructure and the crystalline nature of the Cu_2O nanoparticles were characterized by X-ray diffraction (XRD, Model PW 1710, Philips Co. Ltd., Japan).

2.3. Pretreatment of aluminium electrode

An aluminium sheet (purity 99.99%, thickness 0.3 mm) was used as substrate and it was annealed at 450˚C for a 1/2 hour. The aluminium specimens were mechanically finished by buffing and polishing to get smooth and polished surface. The surface was wiped by sponge soaked in Acetone. The wiping was done in one direction to remove completely the dirt from the surface. Alkaline cleaning was do+ne in 5% (w/v) NaOH for 3-5 minutes at 30ºC. After the treatment, the sample was immediately transferred into running tap water giving up and down movements of the sample for 2-3 minutes. Then the Al electrode was chemically polished in a mixture of concentrated sulfuric, nitric and phosphoric acids. After chemical polishing the electrode were washed thoroughly in a hot water.

2.4. Fabrication of modified electrode

After getting the mirror like surface of aluminium, the deposition of copper was carried out by electrodeposition method. The cleaned surface of electrode is dipped in the solution containing copper sulphate and sulphuric acid. The thickness of copper enclosed on the electrode surface depends on the deposition time of the electrode in the plating solution and the concentration of Copper sulphate in the solution (in this work the plating time varied from 1 to 5 min).

The aluminium electrode enclosed by metallic copper was annealed in an air for an hour at various temperatures. After annealing the modified electrode, metallic copper is converted into a copper oxide and used for electrocatalytic oxidation of ascorbic oxidation. The total surface concentration of the catalyst in the film per unit surface area of the electrode (Γo) was determined from the area under the anodic cyclic

voltammograms of the Copper oxide coated Al electrode**.**

2.5. Characterization of Modified Electrodes

2.5.1. Electrochemical characterization

Cyclic voltammetry and differential pulse voltammetry were performed using CHI 760c electrochemical workstation. A conventional three-electrode system was used with platinum disk act as a counter electrode, calomel as the reference electrode and modified aluminium as the working electrode.

For cyclic voltammetry experiments, the potential was scanned between 1.1 and -0.5 V at a scan rate of 50 mV/s in 0.1 M phosphate buffer. Differential pulse voltammetry (DPV) experiments were performed in the potential range from 1.0 to -0.5 V for the selective determination of ascorbic acid at the pulse amplitude of 50 mV and scan rate of 100 mV/s. All experiments were performed at room temperature.

2.5.2. Reference and counter electrodes

Copper modified aluminium was used as a working electrode. Saturated calomel electrode was used as reference electrode in this investigation. A platinum disk was used as a counter electrode. Pt electrode was cleaned successively with dilute detergent solution, isopropyl alcohol and sodium hydroxide solution. Finally it was rinsed with distilled water.

3. RESULTS AND DISCUSSION

In order to optimize the conditions for getting better CuO coatings, electrodeposition of Copper(I) Oxide on aluminium electrode was carried out at various times. Thickness of the Cu_2O film on aluminium was measured from the mass measurements.

3.1. Characterization of the as-prepared Cu_2O /Al

Fig. 1 shows the typical powder X-ray diffraction (XRD) patterns of the as-deposited Cu_2O films on aluminium electrode. Interplanar distances calculated for (110), (111), (200), (220), (311) and (222) from XRD patterns match well with standard data confirming the formation of a single cubic phase Cu_2O with a cuprite structure. No other diffraction peaks arising from metal Cu or CuO appear in the XRD patterns, which is in good agreement with JCPDS card (No. 78-2076)

3.2. Effect of supporting electrolyte

The redox peaks are dependent on the nature of the cation of the supporting electrolyte. This behavior clearly indicates that the electrolyte cation should be responsible for maintaining the electroneutrality of the electrode surface, thus allowing redox reactions. Six media, namely KCl, phosphate buffer, Britton-Robinson buffer, acetate buffer, sulphuric acid and nitric acid were tested as supporting electrolyte. It was found that KCl and phosphate buffer were outstanding in terms of peak current and sensitivity. Among these two, the best peak was obtained in phosphate buffer. When the concentration of phosphate buffer was 0.25 M, the highest peak was obtained. Thus 0.25 M phosphate buffer was chosen as supporting electrolyte.

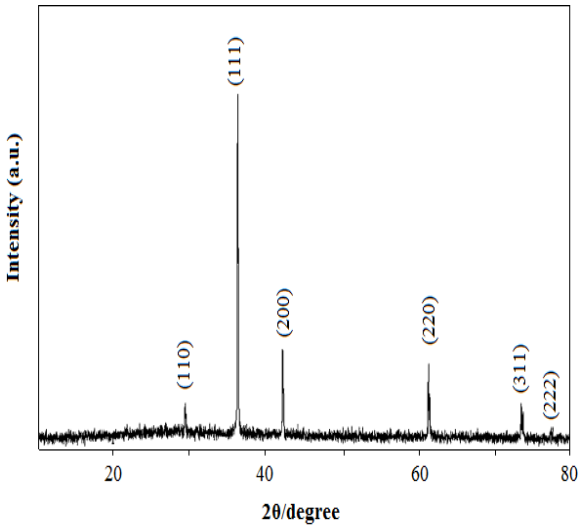


Figure - 1: XRD pattern of the as prepared Cu_2O/Al electrode.

3.3 Electrochemical characterization of the modified electrodes

Electrochemical impedance spectroscopy (EIS) provides detailed information on the change of the surface property of modified electrodes. The impedance spectra includes a semicircle portion and a linear portion. The semicircle diameter at higher frequencies corresponds to the electron transfer limited process or electron-transfer resistance (R_{et}), and this resistance controlled the electron transfer kinetic process of the redox probe on the electrode interface. The linear part at lower frequencies corresponds to the diffusion process. The typical Nyquist diagrams of equivalent $[Fe(CN)_6]^{3-/4-}$ at the bare Al and Cu_2O/Al are illustrated in **Fig. 2**. The R_{ct} of the bare Al is estimated to be 994 Ω cm^{-2}. Later, a further decrease of the Rct (519 Ω cm^{-2}) is observed since the electro-deposition of the Cu_2O, implying that the presence of Cu_2O plays an important role in accelerating the transfer of the electrons, thus decreasing the resistance of the Cu_2O/Al to $Fe(CN)_6^{4-/3-}$. These results indicate that Cu_2O was modified successfully at the surface of aluminium and greatly enhanced the conductivity.

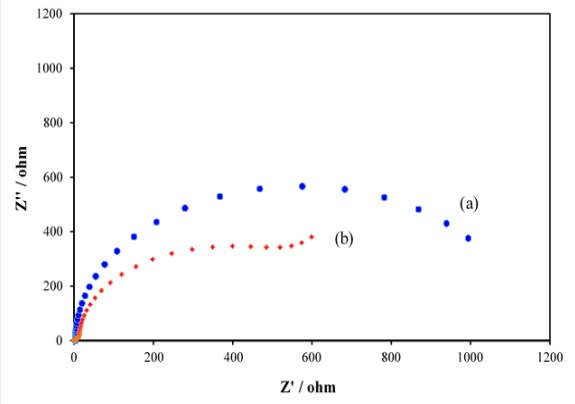


Figure – 2: Nyquist diagrams of (a) Bare aluminium, (b) Cu_2O/Al recorded in 5.0 mM $[Fe(CN)_6]^{3-/4-}$ containing 0.1 M KCl.

3.4 Electro-oxidation of ascorbic acid on Cu_2O nanostructures modified aluminium electrode

Ascorbic acid is the most common electroactive biological compound, being easily oxidized, and this constitutes the basis of its electrochemical determination. Ascorbic acid forms with dehydroascorbic acid an irreversible redox couple. Its electrocatalytical oxidation showed only the anodic oxidation peak [14, 15], for which Randles Sevˇcic equation described the observed direct dependence between the current intensity corresponding to ascorbic acid electrooxidation and the square root of the potential sweep rate [16, 17]. The electrocatalytic property of Cu_2O modified aluminium electrode was investigated by cyclic voltammetry over a potential range from -0.5 to 1.0 V. **Fig. 3** shows the CV of the Cu_2O/Al electrode in 0.25 M phosphate buffer, in the absence and presence of ascorbic acid (1 mM) at a scan rate of 0.1 mV/s. No significant peak current was observed in the absence of AA for the modified electrode and bare aluminium electrode. There is no peak current even in the presence of AA for bare Al electrode. But for the CuO modified Al in the presence of AA, the oxidation started at approximately +0.0 V and a gradual increase in current was observed around +0.10 V, suggesting that Cu_2O have greatly improved the performance of the electrode and increased the electrocatalytic ability towards ascorbic acid oxidation. The oxidation of ascorbic acid to dehydroascorbic acid occurs in the potential range of 0.0 V to 0.4 V, where the oxidation is catalyzed by Cu(I) to Cu(II) conversion [18, 19]. This shows that Cu_2O enabled the electron transfer between ascorbic acid and Al electrode, catalyzed by Cu(II) species, which acted as an electron transfer mediator. Upon addition of 1 mM ascorbic acid, the currents of the electrocatalytic oxidation peaks around at +0.1 V increased in 0.25 M PBS medium. Hence, these experiments strongly support the fact that Cu_2O has good electrocatalytic activity towards the oxidation of ascorbic acid.

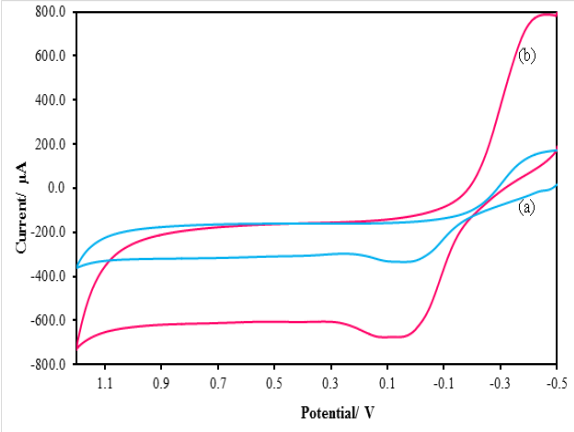


Figure – 3: Cyclic voltammograms of modified electrode (a) in the absence and (b) in the presence of 1 mM ascorbic acid.

3.5 Effect of electrode position time

The thickness of Cu_2O film optimized based on the peak current (Ip). The thickness of the Cu_2O film depends on the deposition time of the electrode in the plating solutions. In the present work, the plating time was varied from 1 to 5 minutes, depending on the desired film thickness. We have found that the optimized electrodeposition time of Cu_2O was 3 minutes. (Fig. 4)

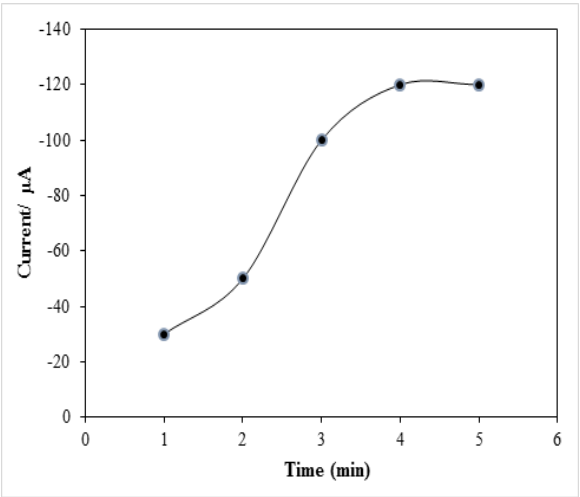


Figure – 4: Effect of deposition time on peak current at Cu_2O modified Aluminium electrode in 0.25 M PBS buffer solution.

This might be associated with an oxidation in the actual working surface area of the electrode that results from excess deposition when larger volumes of Cu_2O film become aggregated on the electrode surface. In light of this possibility, the electrodeposition time of the film selected as 3 minutes for further sensor optimization and study.

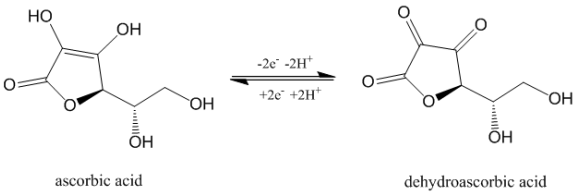
3.6. Effect of pH

The effect of pH on AA was examined in the range of 3.0 to 8.0 at the Cu_2O. From **Fig. 5** it was observed that the anodic peak current increases above pH 5.0. This is because AA exists mainly in the anionic form in solutions at higher pH value (above pH 5.0) and gets stabilized into the deprotonated base [20, 21]. As a result the stronger electrostatic interaction between the deprotonated AA and the modified electrode facilitates the electron transfer reaction [20]. On the other hand, oxidation peak potentials were recorded over the pH range. The peak potential of AA shifts towards the negative value (**Fig. 6**), indicating that protons are involved in the reaction [21]. Thus, the stronger electrostatic interaction between the deprotonated AA and the modified electrode would present an optimized pH at 5.0 corresponding to the maximum oxidation peak current with good sensitivity. Hence, pH 5.0 was selected as a suitable electrolytic medium for further experiments.

$$E_p(3.0 < pH < 8.0) = -0.0669pH + 0.4877$$

which indicates a $2H^+$, $2e^-$ mechanism as it was also reported in a number of previously proposed ascorbic oxidation mechanisms.

Based on these observations, an electrocatalytic mechanism for the oxidation of ascorbic acid by Cu_2O can be expected:



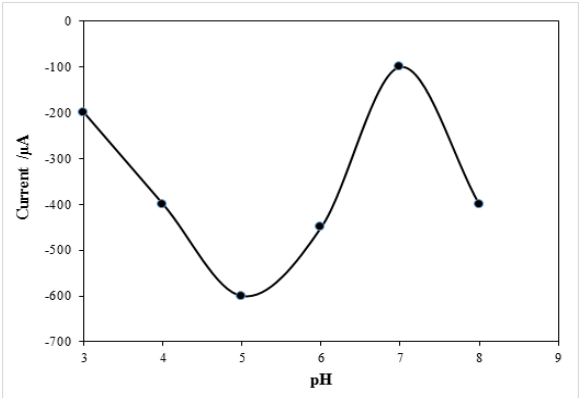


Figure - 5: Effect of pH on peak current at Cu_2O modified Aluminium electrode in 0.25 M PBS buffer solution.

3.7. Effect of accumulation time

For any technique employing preconcentration, the accumulation time is of significant importance for the voltammetric signal. The effect of accumulation time on the peak current of 1 mM AA was investigated by open circuit potential without stirring. The anodic peak current increased within 5 min and then leveled off (**Fig. 7**.). This indicates that the Cu_2O modified electrode is almost saturated with AA after the accumulation for 4 min. from this it can be inferred that a saturation accumulation is reached only after 4 minutes.

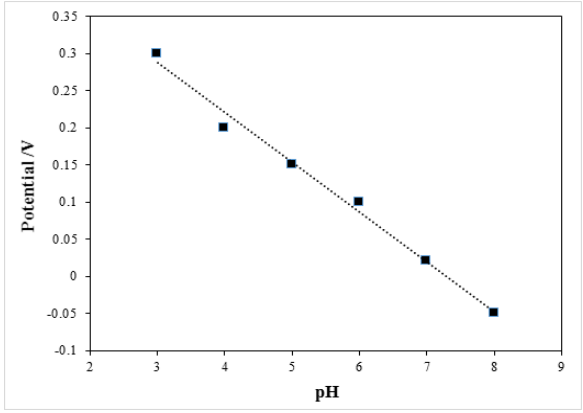


Figure – 6: Effect of pH on peak potential at Cu_2O modified Aluminium electrode in 0.25 M PBS buffer solution.

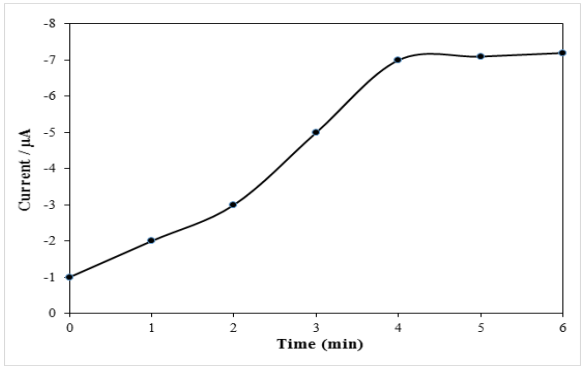


Figure – 7: Effect of accumulation time on peak current at Cu2O modified aluminium electrode in 0.25 M PBS buffer solution.

3.8. Effect of scan rate

Fig. 8 shows the effect of different scan rates on the electrochemical oxidation of AA at the Cu_2O. From Fig.9 (a) and (b), it was observed that as the potential scan rate increases the anodic peak current increases, resulting in a shift in the anodic peak potential towards a more positive value for electrochemical oxidation of AA. Similar kinds of results were observed by Raoof et al. [22] for the electrochemical oxidation of AA at a modified carbon paste electrode. This shift in the anodic peak potential gives a clear idea about the irreversible electrochemical process at the electrode surface [23]. The anodic peak current increases linearly with the increase in the square root of scan rate at Cu_2O as shown in Fig. 9(a). This suggests that the electron transfer reaction is

diffusion controlled [24, 25]. For a totally irreversible diffusion controlled process, the following equation can be used to calculate the Tafel slope, b, for the rate determination step:

$$E_p = \left(\frac{1}{2}\right) b \log \upsilon + constant$$

where b is the Tafel slope and y is the scan rate (mV s^{-1}). From eqn (1), the slope of Ep vs. log υ is b/2, which was found to be 0.0972 V from Fig. 9 (b) and therefore b becomes 0.1944 V (b/2=0.0972).

The Tafel slope can also be expressed in another form

$$b = 2.303RT/(\alpha nF)$$

where a is the charge transfer coefficient, n is the number of electrons transferred and F is the Faraday constant. Oxidation of AA is a two electron transfer process [26]. Therefore, n = 2, F=96480 and b = 0.1944. Substituting these values in eqn (2) gives the numerical value for the charge transfer coefficient (a) and is equal to 0.1521.

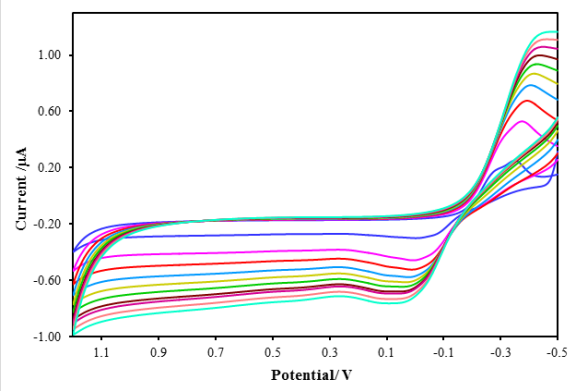


Figure – 8: Cyclic voltammograms obtained for 1 mM ascorbic acid in PBS (pH 7.0) at different scan rates (10-100 mV s^{-1}).

3.9. Differential pulse voltammetric (DPV) studies

The Differential pulse voltammograms technique is one the most sensitive and high resolution techniques compared to the CV technique in order to examine the electrochemical behavior of reactant molecules which are bound to the electrode surface [27, 28]. DPV recorded for various ascorbic acid concentrations at the Cu_2O/Al (Figure 10 (a)) showed a linear variation of the peak current intensity with ascorbic acid concentration in the range of 5 x 10^{-6} mol/L to 110 x 10^{-6} mol/L in phosphate buffer (pH = 4.0). The linear regression (Figure. 10) equation was expressed as:

$$Ipa(\mu A) = -7Conc_{ascobic\ acid}\ (\mu M) + 0.0012 \quad R2 = 0.9984$$

Ten repeat voltammetric experiments were carried out at the lowest ascorbic acid concentration and the standard deviation (s) of the measured currents was calculated. By interpolating a current value of intercept +3 s (corresponding to an S/N certainty of 99.8%) into the calibration equation given in Fig. 10 (b) we obtained a detection limit of 0.5 µM ascorbic acid. Hence, it can be concluded that the Cu_2O modified aluminium electrode show excellent sensitivity and lower detection limit for ascorbic acid.

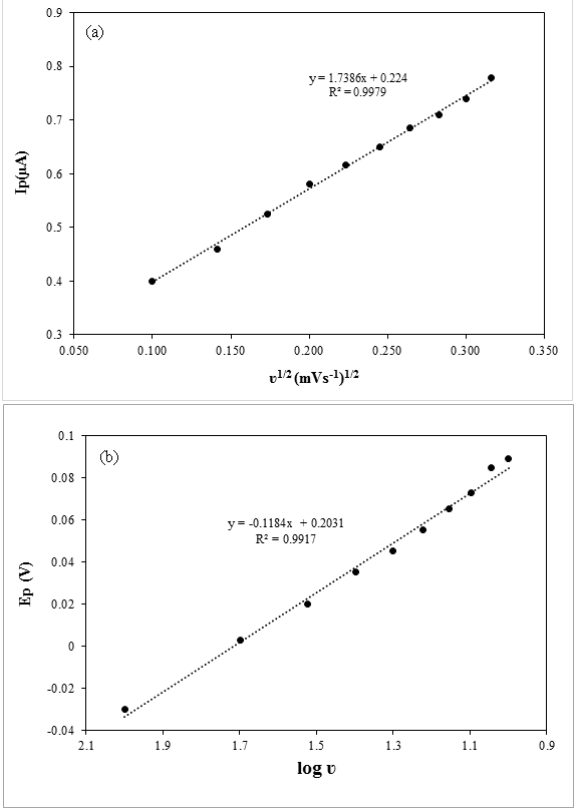


Figure – 9: (a) Influence of square root of scan rate on anodic peak current. (b). Calibration plot of potential vs. logarithmic scan rate.

3.10. Stability of the modified electrode

The stability of the Cu_2O-deposited aluminium electrode toward various influences was also examined and was found satisfactory. There were no changes in the height and separation of the cyclic voltammograms after 100 cycles of repetitive scanning in 0.25 M phosphate buffer solution.

3.11. Reproducibility

After each measurement, the modified electrode was washed with distilled water and the adsorbed ascorbic acid was removed by performing 5–10 cyclic voltammograms in the supporting electrolyte in the working potential window. The reproducibility of Cu_2O/Al was estimated by comparing the oxidation peak current obtained for 10 determinations on a 2 x

10^{-6} mol L^{-1} ascorbic acid solution in PBS. The relative standard deviation (RSD) of 3.4% (n = 10) revealed a good reproducibility of the method.

3.12. Interference study

In the present work, the interference effects of 0.1 mM uric acid (UA), 10 µM dopamine (DP) and 1 mM glucose (Glu), adenine (ad) were tested on the voltammetric response of 5 mM ascorbic acid. In the mixture of all these compounds by using the modified electrode, five well-defined waves with a very good resolution are resulted. Among these interferences, glucose has no response but UA, and DP showed oxidation process in the selected potential range. Therefore, in this study it was proved that this method can be successfully applied for determination of ascorbic acid in the presence of the other interference compounds in the clinical preparations.

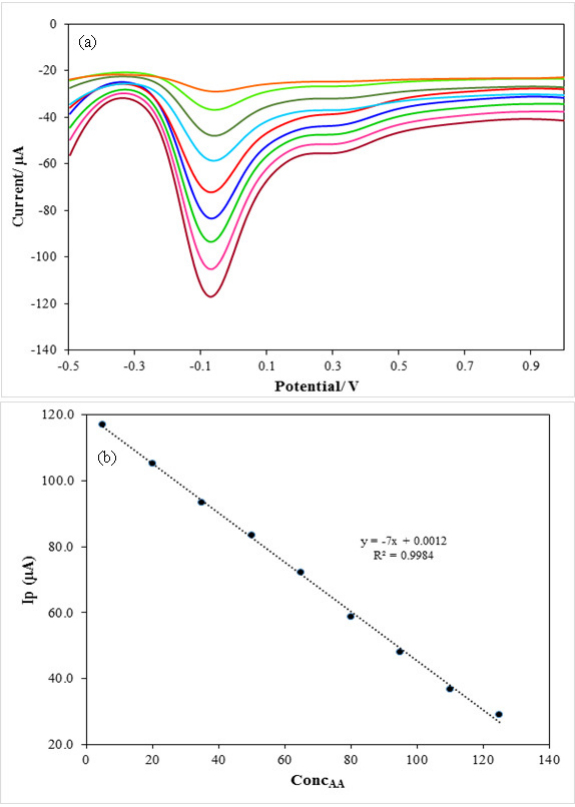


Figure – 10: (a) Differential pulse voltammograms of different concentrations of ascorbic acid at Cu_2O (5 – 125 µM). (b) Calibration plot of peak current (Ip) vs. Concentration of ascorbic acid.

4. CONCLUSION

Electrochemical sensor technology is still limited in scope, and hence cannot solve all experimental monitoring needs. Yet, a vast array of electrochemical sensors has been applied in recent years for monitoring a wide range of drugs and biological molecules. Electrocatalytic oxidation of ascorbic acid using an electrochemical sensor Copper oxide modified aluminium electrode has been investigated at various electrodeposition time of Cu_2O, accumulation time, pHs, scan rates and detection limit. In this work, the electrocatalytic activity of Cu_2O-modified aluminium electrode toward the oxidation of ascorbic acid in phosphate buffer medium was demonstrated. Well-defined oxidation peak potential of Cu_2O that appears in phosphate buffer medium can electrocatalyze and improve dramatically the oxidation signal of ascorbic acid. The optimized pH was 5.0 at Cu_2O modified aluminium from peak current obtained in cyclic voltammetry. An electrocatalytic possible mechanism for the oxidation of ascorbic acid by Cu_2O on aluminium electrode derived satisfactory. From the differential pulse voltammetry, detection limit was found to be 0.5 µM. Comparing this sensor with those reported previously, it can be pointed out that a big advantage of aluminium like electrode materials is the ease of modification in order to obtain higher selectivity, to lower the overpotential, or to achieve lower limits of detection and a wider range of linear response toward the analyte.

Acknowledgements

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5. REFERENCES

1. A. Hodgkinson, Oxalic acid in biology and medicine, Academic Press, London, UK, 1977.
2. J. Wawrzyniak, A. Ryniecki, W. Zembrzuski, Acta Sci. Pol.Technol Aliment. 42 (2005) 5.
3. A. Carr, B. Frei, FASEB J. 13 (1999) 1007.
4. M. Valko, H. Morris, M.T. Cronin, Curr. Med. Chem. 12 (2005) 1161.
5. F. Caruso, Adv. Mater. 13 (2001) 11.
6. P. Pandey, M. Datta, B. D. Malhotra, Anal. Lett. 41 (2008) 159.
7. C. Jianrong, M. Yuqing, H. Nongyue, W. Xiaohua, L. Sijiao, Biotechnol. Adv. 505 (2004).
8. M.H. Cao, C.W. Hu, Y.H. Wang, Y.H. Guo, C.X. Guo, E.B. Wang, Chem. Commun. 15 (2003) 1884.
9. M. Vaseem, A. Umar, S.H. Kim, Y.B. Hahn, J. Phys. Chem. C 112 (2008) 5729.
10. J.T. Zhang, J.F. Liu, Q. Peng, X. Wang, Y.D. Li, Chem. Mater. 18 (2006) 867.
11. W. Jia, M. Guo, Z. Zheng, T. Yu, Y. Wang, E. Rodriguez, Y. Lei, Electroanalysis (2008), doi:10.1002/elan.200804299.

12. G.L. Luque, M.C. Rodriguez, G.A. Rivas, Talanta 66 (2005) 467.
13. C.B. McAuley, Y. Du, G.G. Wildgoose, R.G. Compton, Sens. Actuators, B: Chem. 135 (2008) 230.
14. C.S. Erdurak-Kilic¸, B. Uslu, B. Dogan, U. Ozgen, S.A. Ozkan, M. Coskun, J. Anal. Chem. 61 (2006) 1113
15. R.N. Adams, Anal. Chem. 48 (1976) 1126A.
16. S. Senthil Kumar, J. Mathiyarasu, K.L.N. Phani, V. Yegnaraman, J. Solid State Electrochem. 10 (2006) 905.
17. A.F. Danet, Electrochemical methods of analysis, Editura Stiintifica, Bucharest, 1996.
18. Zhang L, Li H, Ni Y, Li J, Liao K and Zhao G, Electrochem. Commun. 11 (2009) 812.
19. Qian Y, Ye F, Xu J and Le Z G, Int. J. Electrochem. Sci. 7 (2012) 10063
20. B. Habibi, M. Jahanbhaskhi and M. H. Pournaghi-Azar, Anal. Biochem., 411 (2011) 167–175.
21. C. Y. Li, Y. J. Cai, C. H. Yang, C. H. Wu, Y. Wei, T. C. Wen, T. L. Wang, Y. T. Shieh, W. C. Lin and W. J. Chen, Electrochim. Acta, 56 (2011) 1955–1959.
22. J. B. Raoof, R. Ojani and S. Rachid-Nadimi, Electrochim. Acta, 49 (2004) 271–280.
23. C. de la Fuente, J. A. Acuna, M. D. Vasquez, M. L. Tascon, M. I. Gomez and P. S. Batanero, Talanta, 44 (1997) 685–695.
24. M. R. Akhgar, M. Salari and H. Zamani, J. Solid State Electrochem., 15 (2011) 845–853.
25. H. Karimi-Maleh, M. A. Khalilzadeh, Z. Ranjbarha, H. Beitollahi, A.A.Ensafi and D.Zareyee, Anal. Methods, 2012, 4(7), 2088–2094.
26. B. Habibi, M. Jahanbhaskhi and M. H. Pournaghi-Azar, Anal. Biochem., 411 (2011) 167–175.
27. A. J. Bard and L. R. Faulkner, Electrochemical Methods: Fundamentals and Applications, Wiley, New York, 2nd edn, 2001, p. 240.
28. W. R. Heineman and P. T. Kissinger, Anal. Chem., 50 (1978) 166.