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Original scientific paper

Determination of ascorbic acid at solid electrodes modified with L-cysteine

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Abstract

Gold and glassy carbon electrode surfaces were modified with L-cysteine, and the electrochemical behavior of ascorbic acid (AA) was investigated on these new surfaces. To improve the efficiency of electrodes, the electrode surfaces were modified and optimum conditions for AA determination were established. Electrochemical experiments were performed at different potential ranges, the concentration of AA, scan rates, number of polymerization cycles and pH values. Using cyclic voltammetry (CV) technique, optimum conditions were determined as the potential scanning range of 0.2 to 1.5 V vs. *Ag/AgCl in 0.1 M phosphate buffer solution (pH 7.02) for the L-cysteine/Au electrode, and -1.95 to 1.9 V* vs. *Ag/AgCl in 0.1 M phosphate buffer solution (pH 2.7) for the L-cysteine/GC electrode. For the characterization of both modified electrode surfaces, a series of physicochemical techniques was also applied. The usability and selectivity of these two proposed modified electrodes for the determination of AA were investigated using square wave voltammetry (SWV) in the presence of possible interferents,* i.e., *glycine, L-glutamic acid and uric acid.*

Keywords

Modified electrodes; electropolymerization; poly(L-cysteine); voltametric sensor; vitamin C

Introduction

Ascorbic acid, an important water-soluble vitamin, has many names, such as antiscorbutic vitamin, L-ascorbic acid, and vitamin C [1,2]. Ascorbic acid is necessary for the production of collagen, an important protein for the structure of muscles, bones, blood vessels and cartilage in the body [3]. The concentration of ascorbic acid in foods and pharmaceuticals is extremely important for determining the quality in the production and storage steps [4]. Different techniques are usable for AA determination, such as chromatography [5], potentiometric titration [6], voltammetry [7], conductometry [8], titrimetry [9], amperometry [10], fluorometry [11], flow-injection analysis (FIA) [12] and chemiluminescence [2]. The various voltammetric techniques, however, showed some advantages such as a very large linear concentration range for both inorganic and

organic species, high sensitivity, ability to work with a large number of solvents and electrolytes, ability to work in a wide temperature range, rapid analysis times, determination of several analytes at the same time, and ability to determine kinetic and mechanistic parameters [13].

At standard solid electrodes, the determination of ascorbic acid is not very reliable due to low sensitivity and poor reproducibility. Therefore, it has become important to modify the electrode surface with different materials, such as gold nanoparticles [14], ruthenium oxide [15], chitosan [16] and poly(L-cysteine) film [3].

Amino acids, the most basic substances of the organism, contain amino and carboxyl functional groups. Because of its versatility and ease of preparation, poly(L-cysteine) is widely used to prepare voltammetric sensors [17]. The main objective of this work was to manufacture modified glassy carbon (GC) and gold (Au) electrodes for the determination of ascorbic acid using poly(L-cysteine) film. Both electrochemical performance and surface characterization of Au and GC electrodes modified with poly(L-cysteine) are performed by voltammetry and SEM and TEM techniques.

Experimental

Chemicals and reagents

In this study, the chemicals obtained from the related companies were used directly without a purification process. Sodium dihydrogen phosphate (NaH_2PO_4), sodium dihydrogen phosphate dihydrate ($NaH_2PO_4{\cdot}2H_2O$), and sodium acetate trihydrate ($C_2H_3NaO_2{\cdot}3H_2O$) were supplied from VWR. Sodium chloride (NaCl), sulfuric acid (H_2SO_4), ortho-phosphoric acid (85 %), boric acid, citric acid monohydrate, and ferrocene ($C_{10}H_{10}Fe$) were supplied from Merck. Tetrabutylammonium tetrafluoroborate (TBATFB) (99 %) was supplied from Sigma-Aldrich. Acetonitrile (CH_3CN) (≥ 99.9 %) was supplied from Isolab. Glycine (99 %), uric acid (99 %), l-glutamic acid (99 %), potassium hexacyanoferrate (II) trihydrate ($K_4[Fe(CN)_6]{\cdot}3H_2O$), and potassium hexacyanoferrate (III) ($K_3[Fe(CN)]_6$) were supplied from Alfa Aesar. Sodium hydrogen phosphate (Na_2HPO_4) and l (+) ascorbic acid were supplied from (John Townsend Baker, Gliwice, Poland). Potassium chloride (KCl) and acetic acid (CH_3COOH) were supplied from Riedel-de Haén. L-cysteine was supplied from Acros Organics and stored at 4 °C. Aluminum oxide (Al_2O_3) was supplied from Nanografi Company. Ultra-pure water and freshly prepared solutions were used throughout the experiment. All solutions were stored in the refrigerator. The solution of L-cysteine used for surface coating was prepared in the phosphate buffer solution.

Instrumentation and other equipment

Gamry Reference 600 and Series G 750 potentiostat/galvonastat/ZRA devices were used in the electrochemical examination of experiments. Bioanalytical system (BAS) C3 cell system was used, which includes the working (BAS model MF-2012 GC and BAS model MF-2013 Au), reference Ag/AgCl/(sat. KCl)) used in aqueous media, or Ag/Ag^+ (in 10 mM $AgNO_3$), used in non-aqueous media) and counter (platinum wire) electrodes.

Scanning electron microscopy and transmission electron microscopy analyses were carried out at Selcuk University - Advanced Technology Research and Application Center.

During the study, special care was taken that the calibration of all used devices was done at certain time periods. Bandelin RK 100 model ultrasonic bath was used for cleaning electrode surfaces. JENWAY 3010 model pH meter was used at room temperature for pH adjustments of prepared solutions. Argon gas was passed through the solutions for at least 3 minutes prior to experiments.

Preparation of modified working electrode

Firstly, bare electrode surfaces were electrochemically cleaned by cyclic voltammetry at -0.2 / +1.5 V (10 cycles) in 0.1 mol dm^{-3} H_2SO_4 solution. After that, electrodes were washed with pure water and cleaned in a circular direction with the suspension of alumina polishing powder of 0.3 and 0.05 µm dimensions on the velvet surface. At the end of the alumina powder process, electrodes were sonicated in pure water and acetonitrile for three minutes, respectively [18,19]. Modified solid contact electrodes with poly(L-cysteine) were prepared by potentiodynamic polymerization. Electropolymerization of L-cysteine on the GCE surface was performed by 25 potential cycles at the scan rate of 150 mV/s between -1.95 and 1.9 V in pH 2.7 phosphate buffer containing 30 mmol dm^{-3} L-cysteine (Figure 1). Electropolymerization of L-cysteine on the Au electrode surface was performed by 25 potential cycles at 150 mV/s between 0.2 and 1.5 V in pH 7.02 phosphate buffer solution containing 1.0 mmol dm^{-3} L-cysteine (Figure 2). Prepared electrodes were named L-cysteine/Au and L-cysteine/GC, respectively.

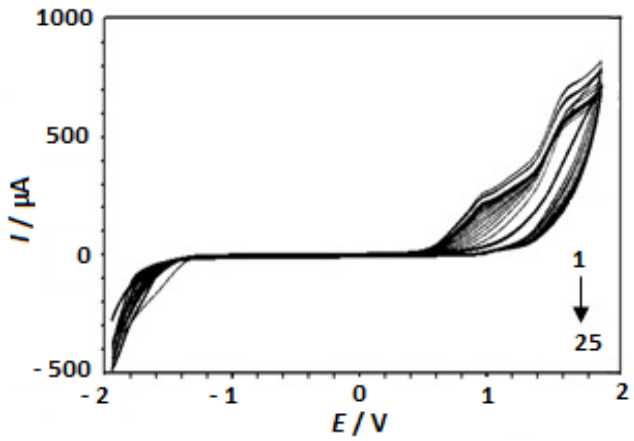


Figure 1. *Electropolymerization of 30 mmol dm^{-3} L-cysteine on the GCE surface with cyclic voltammetry between -1.95 and 1.9 V at 25 cycles in pH 2.7 phosphate buffer solution (scan rate: 150 mV/s)*

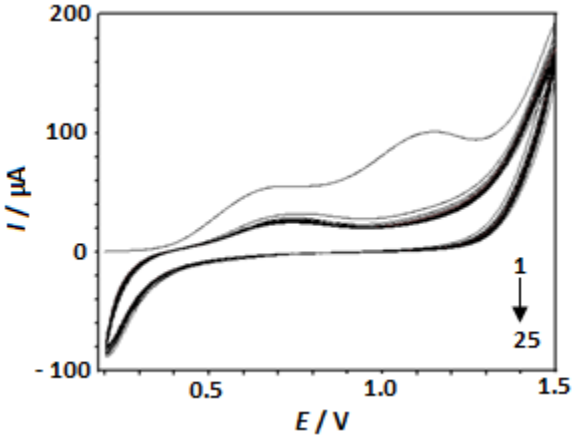


Figure 2. *Electropolymerization of 1 mmol dm^{-3} L-cysteine on the Au electrode with cyclic voltammetry between 0.2 and 1.5 V at 25 cycles in pH 7.02 phosphate buffer solution (scan rate: 150 mV/s)*

Surface characterization of prepared electrodes

L-cysteine/Au, L-cysteine/GC and clean (bare) electrode surfaces were characterized by CV in the presence of redox probes. Investigation of surface properties of electrodes was carried out with the CV technique in the presence of 1.0 mmol dm^{-3} of ferrocene as redox-active species in CH_3CN solution containing 0.1 mol dm^{-3} of TBATFB. Surface images and analysis of L-cysteine/Au, L-cysteine/GC and clean (bare) electrodes were investigated with SEM and TEM at Selçuk University - Advanced Technology Research and Application Center.

Results and discussion

Cyclic voltammetry

Figures 1 and 2 show that the peaks in the first cycle decreased in the subsequent cycles of L-cysteine polymerization. As a reason, it was thought that the film layer of poly(L-cysteine) formed on the electrode surfaces does not allow electron exchange.

Electrochemical probes were used in the characterization process of modified electrode surfaces [20,21]. Voltammograms of bare and modified electrodes were taken using the cyclic voltammetry

technique in 1.0 mmol dm^{-3} ferrocene solution as a redox probe in CH_3CN containing 0.1 mol dm^{-3} of TBATFB. The recorded voltammograms can be compared in Figures 3 and 4.

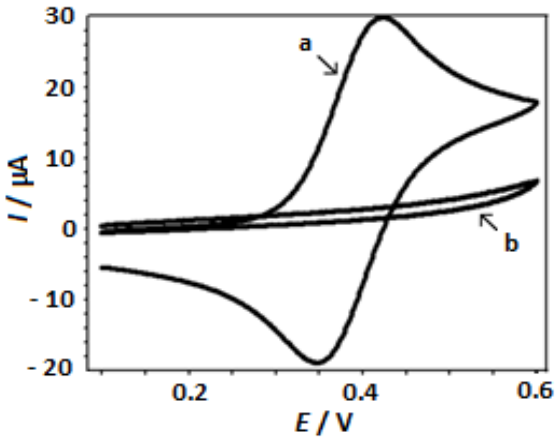


Figure 3. *Comparison of voltammograms of (a) bare and (b) L-cysteine/GC electrodes in 1.0 mmol dm^{-3} ferrocene solution (in CH_3CN containing 0.1 mol dm^{-3} of TBATFB)*

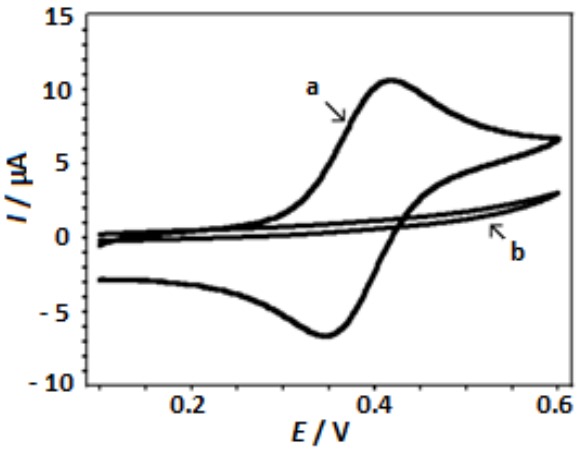


Figure 4. *Comparison of voltammograms of (a) bare and (b) L-cysteine/Au electrodes in 1.0 mmol dm^{-3} ferrocene solution (in CH_3CN containing 0.1 mol dm^{-3} of TBATFB)*

It is seen in Figures 3 and 4 that almost reversible oxidation and reduction peaks of the ferrocene/ferrocenium (Fc/Fc^+) redox couple, characteristic for bare GC and Au electrodes, cannot be observed for both L-cysteine/GC and L-cysteine/Au electrode surfaces. These suggest that modified electrode surfaces do not allow electron transfer, while bare GC and Au electrode surfaces allow electron transfer. It seems that rather different surfaces were obtained after 25 cycles of polymerization of L-cysteine, which resulted in poly(L-cysteine) molecules attached to the surface of the electrodes [22,23].

Scanning electron microscopy

The surface images of electrode surfaces were taken with the scanning electron microscopy technique in order to see the surface morphology of electrodes and observe physical changes on the electrode surfaces [24] (Figure 5).

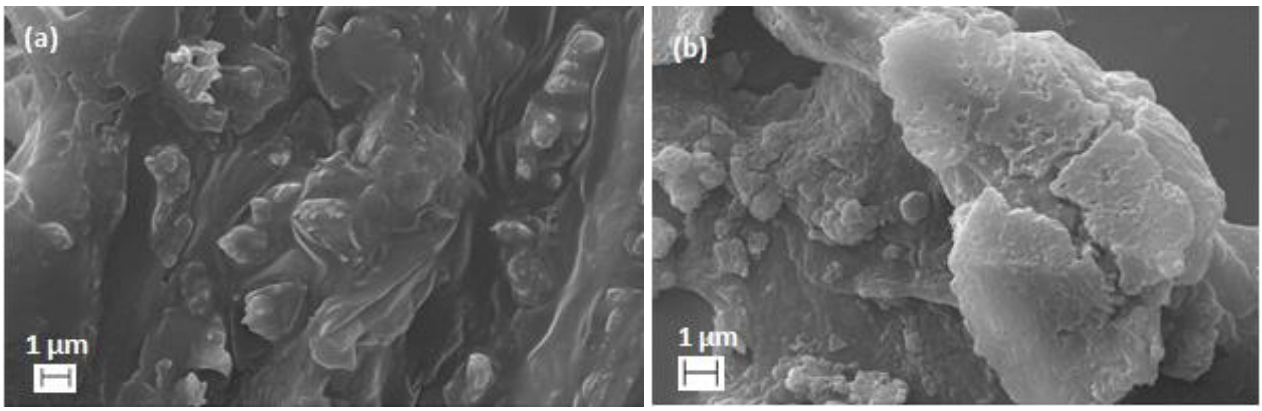


Figure 5. *Scanning electron microscopy images of (a) L-cysteine/GC and (b) L-cysteine/Au electrodes*

When the SEM images of the electrode surfaces were compared, it was seen that the surface images were different, but both images proved that electrode surfaces are modified with L-cysteine.

Transmission electron microscopy

The morphology of electrode surfaces modified with L-cysteine was also investigated by TEM studies. As seen in Figure 6, L-cysteine is dispersed over the surfaces of both electrodes [25,26].

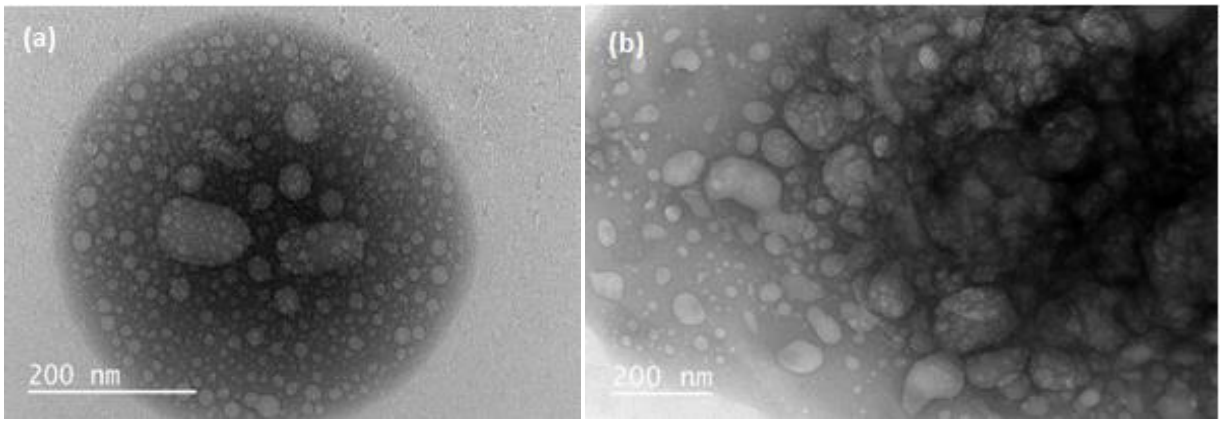
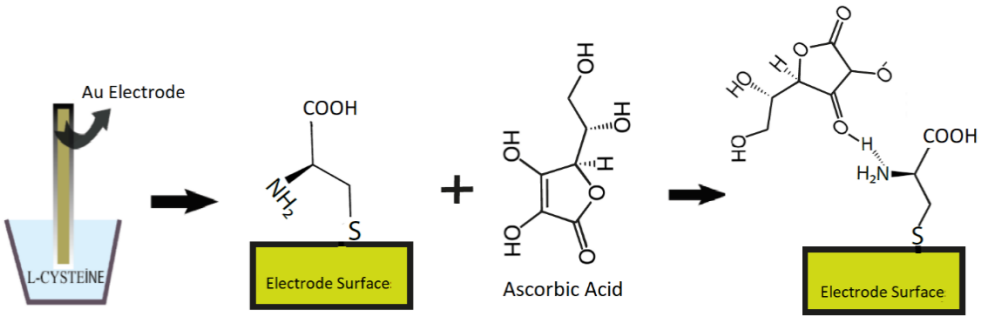


Figure 6. *Transmission electron microscopy images of (a) L-cysteine/GC and (b) L-cysteine/Au electrodes*

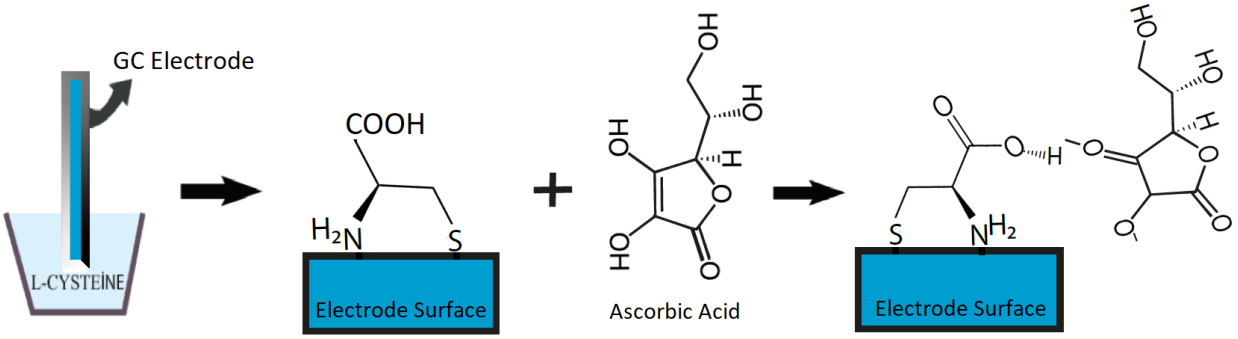
Electrochemical behavior of ascorbic acid

Scheme 1 shows that the L-cysteine is attached to the electrode surface *via* sulfur atoms. It is also known from the literature that the sulfur atom is very well attached to the voids on the gold surface [27]. Modification of the Au electrode by L-cysteine and the predicted binding pattern of ascorbic acid (AA) to the modified electrode surface are shown in Scheme 1.



Scheme 1. *Modification of Au electrode surface by L-cysteine and the estimated bonding pattern of AA to the modified electrode surface*

Scheme 2 shows that L-cysteine is attached to the surface of the GCE with sulfur and nitrogen atom. Since the sulfur atom did not provide good adhesion to the C atoms of the electrode, the nitrogen atom also affects the attachment. The modification of the GCE surface by L-cysteine and the estimated binding pattern of ascorbic acid (AA) to the modified electrode surface are shown in Scheme 2.



Scheme 2. *Modification of GCE surface by L-cysteine and the estimated bonding pattern of AA to the modified electrode surface*

Figure 7 and Figure 8 show cyclic voltammograms of 3.0 mmol dm^{-3} ascorbic acid (AA) prepared in phosphate buffer solution using modified GC and Au electrodes in comparison with bare electrodes.

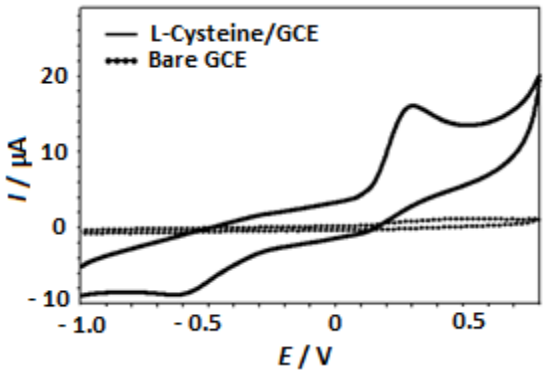


Figure 7. *Cyclic voltammograms of 3.0 mmol dm^{-3} AA on bare GC and L-cysteine/GC electrode surfaces in phosphate buffer medium (pH 5.0)*

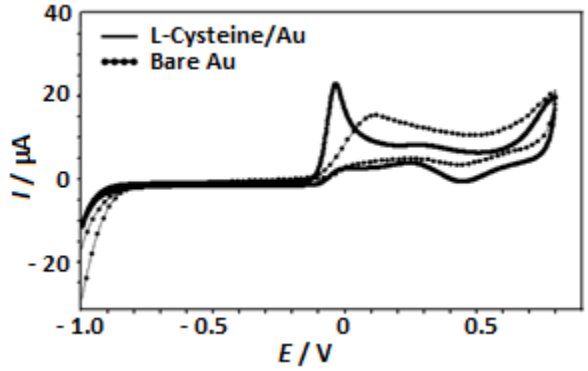


Figure 8. *Cyclic voltammograms of 3.0 mmol dm^{-3} AA on bare Au and L-cysteine/Au electrode surfaces in phosphate buffer medium (pH 7.02)*

From voltammograms presented in Figures 7 and 8, much higher peak current values for ascorbic acid can be observed on the modified electrodes compared to bare electrodes. This suggests that, in this way, the amount of ascorbic acid can be determined using modified electrodes. In addition, the peak potential of ascorbic acid is shifted to a lower value, indicating the electrocatalytic effect of L-cysteine [28].

In a set of experiments (not shown here), a scan rate study was performed to determine whether the reaction of ascorbic acid on L-cysteine-modified electrode surfaces is diffusion-controlled or adsorption-controlled. For this purpose, cyclic voltammograms of 3.0 mmol dm^{-3} ascorbic acid at different scanning rates between 5 and 500 mV/s were taken. The slope value of the log I_p *vs.* log v graphs gives information on either diffusion or adsorption control of the redox processes. It indicates that the reaction on the modified surface is not diffusion-controlled if the slope values are different from 0.5 [22,29]. In this study, it was observed that the reaction on the modified electrode surfaces was not diffusion-controlled since the slope values were different from 0.5. The fact that the reaction of AA at both modified electrode surfaces is not diffusion-controlled approves mechanisms drawn in Schemes 1 and 2.

The analytical performance of modified electrodes has also been studied. The effect of ascorbic acid concentration on electrode surfaces modified with L-cysteine using square wave voltammetry (SWV) is shown in Figures 9 and 10. Both SW voltammograms show that the peak currents of ascorbic acid increased with the increase of the ascorbic acid concentration, meaning that both modified electrodes could serve for the evaluation of AA.

Interference study

For determination of electrode selectivity, the modified electrode surfaces under optimum conditions were tested in solutions containing ascorbic acid (AA), glycine (GLY), L-glutamic acid (GA) and uric acid (UA). For a selectable and objective comparison, all solutions were prepared at the concentration of 3.0 mmol dm^{-3} and tested by the cyclic voltammetry technique in the scanning range of -1.0 to 0.8 V at the scanning speed of 100 mV/s (Figures 11 and 12).

The most important feature of the prepared high-performance sensors is their selectivity. At the bare GC electrode (Figure 11a), ascorbic acid (AA), glycine (GLY), L-glutamic acid (GA) and uric acid (UA) showed oxidation peaks. Since oxidation peak potentials are close to each other, it is difficult to distinguish them from each other.

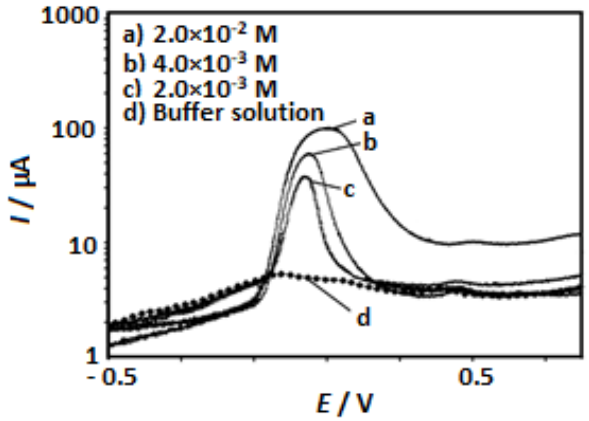


Figure 9. *Effect of concentration of ascorbic acid using square wave voltammetry recorded on L-cysteine/GC electrode*

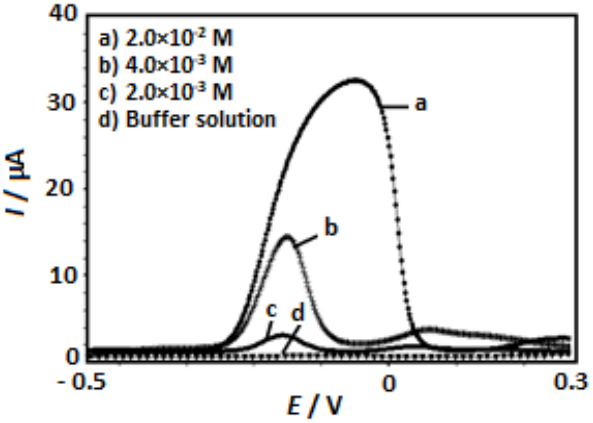


Figure 10. *Effect of concentration of ascorbic acid using square wave voltammetry recorded on L-cysteine/Au electrode*

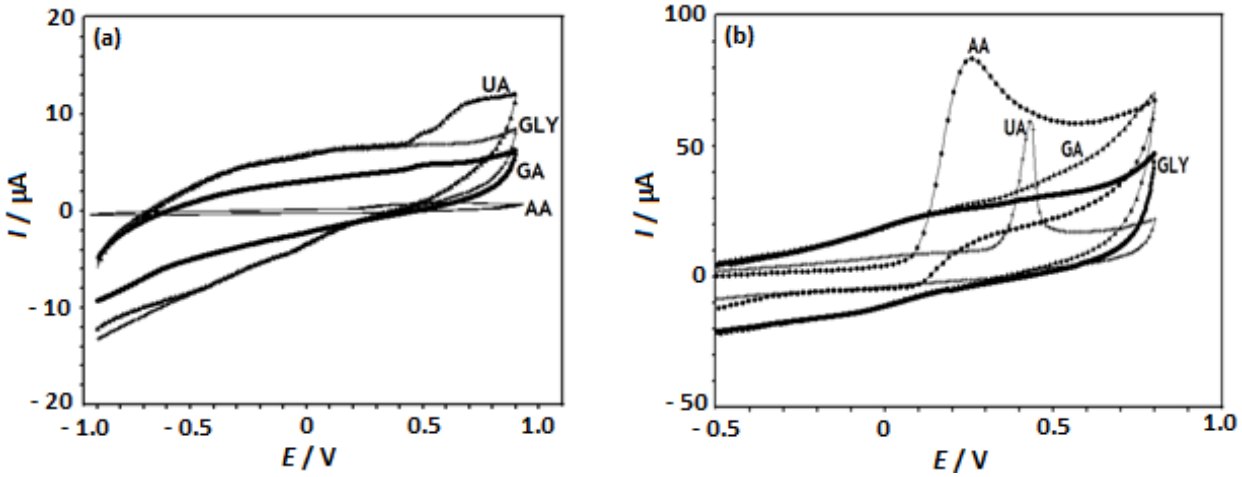


Figure 11. *Cyclic voltammograms recorded at: (a) bare GC electrode, (b) L-cysteine/GC electrode in 3.0 mmol dm^{-3} ascorbic acid (AA), 3.0 mmol dm^{-3} glycine (GLY), 3.0 mmol dm^{-3} L-glutamic acid (GA) and 3.0 mmol dm^{-3} uric acid (UA) solutions*

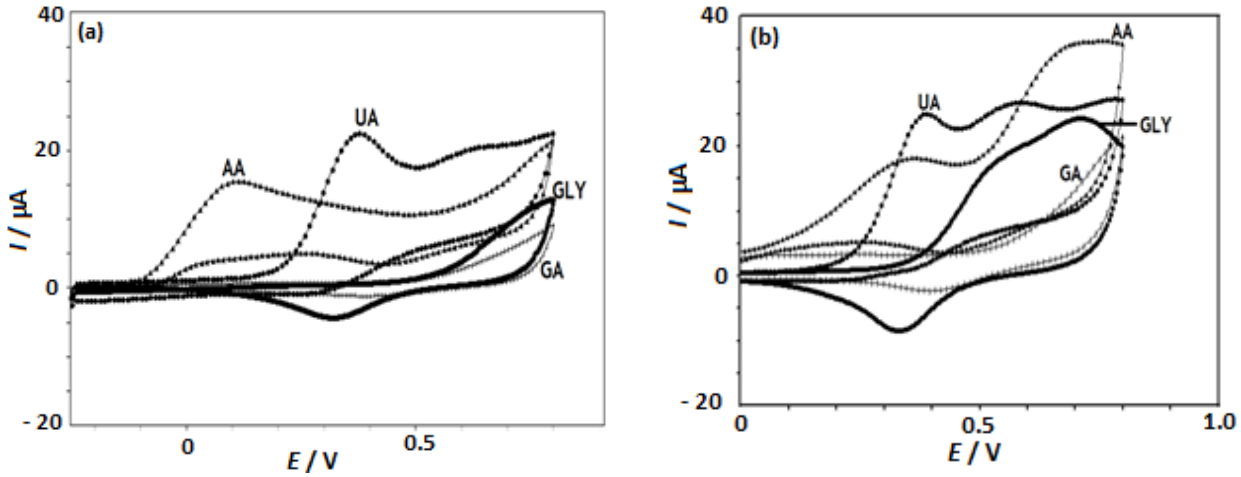


Figure 12. *Cyclic voltammograms recorded at: (a) bare Au electrode, (b) L-cysteine/Au electrode in 3.0 mmol dm^{-3} ascorbic acid (AA), 3.0 mmol dm^{-3} glycine (GLY), 3.0 mmol dm^{-3} L-glutamic acid (GA) and 3.0 mmol dm^{-3} uric acid (UA) solutions*

In the case of the GC electrode modified with the L-cysteine (Figure 11b), the potentials of ascorbic acid and uric acid oxidation were-different from those monitored at the bare GC electrode.

Also, an increase in the peak current of ascorbic acid was observed when compared to the bare GC electrode. At the bare Au electrode (Figure 12a), ascorbic acid, glycine, L-glutamic acid and uric acid showed oxidation peaks. In the case of the Au electrode modified with the L-cysteine (Figure 12b), the potentials of ascorbic acid and glycine oxidation were different from those monitored at the bare Au electrode. Also, an increase in the peak current of ascorbic acid was observed when compared to the bare gold electrode. The modified electrodes could also inhibit redox currents of glycine and L-glutamic acid, significantly reducing the current responses. Due to the difference in oxidation peak potentials for ascorbic acid and uric acid in the modified electrodes, these electrodes can be expected to separate the oxidation peak potentials in the same solution with coexisting ascorbic acid and uric acid.

Conclusions

In this study, glassy carbon and gold electrodes modified with electropolymerized L-cysteine were used for the determination of ascorbic acid. As the concentration of ascorbic acid in foods and drugs is extremely important for the determination of quality in the production and storage stages, it is important to develop a method for the determination of ascorbic acid. Electrode modification was performed in an extremely simple and fast method. The proposed sensors (L-cysteine/GC and L-cysteine/Au) provided sensitivity, selectivity, short measurement time, ease of preparation and good analytical performance. Morphological changes on the electrode surfaces and the existence of poly (L-cysteine) were proven by SEM and TEM analyses. It was determined by the SWV technique that the sensitivity to ascorbic acid was increased by modifying electrode surfaces. The modified electrodes showed good selectivity in the presence of interferents.

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References

[1] E. K. Janghel, S. Sar, Y. Pervez, A new method for determination of ascorbic acid in fruit juices, pharmaceuticals and biological samples, *Journal of Scientific and Industrial Research* **71** (2012) 549-555. http://nopr.niscair.res.in/bitstream/123456789/14525/1/JSIR%2071%288%29%20549-555.pdf

[2] C. K. Pires, A. F. Lavorante , L. M. T. Marconi, S. R. P. Meneses, E. A. G. Zagatto, A multi-pumping flow system for chemiluminometric determination of ascorbic acid in powdered materials for preparation of fruit juices, *Microchemical Journal* **83(2)** (2006) 70-74. https://doi.org/10.1016/j.microc.2006.02.001

[3] X. Zheng, D. Zhou, D. Xiang, W. Huang, S. Lu, Electrochemical determination of ascorbic acid using the poly-cysteine film-modified electrode, *Russian Journal of Electrochemistry* **45(10)** (2009) 1183-1187. https://doi.org/10.1134/S1023193509100115

[4] R. Barsbuğa, Determination of uric acid using aluminium oxide nanoparticles modified carbon paste electrode in the presence of ascorbic acid. *MSc Thesis*, *Namık Kemal University*, Tekirdağ, Turkey, 2016. http://acikerisim.nku.edu.tr:8080/xmlui/bitstream/handle/20.500.11776/1096/0050095.pdf?sequence=1&isAllowed=y

[5] D. Ivanović, A. Popović, D. Radulović, M. Medenica, Reversed-phase ion-pair HPLC determination of some water-soluble vitamins in pharmaceuticals, *Journal of Pharmaceutical and Biomedical Analysis* **18(6)** (1999) 999-1004. https://doi.org/10.1016/S0731-7085(98)00109-5

[6] G. S. Sastry, G. G. Rao, Oxidimetric determination of ascorbic acid with potassium hexacyanoferrate(III) in acid medium, *Talanta* **19(2)** (1972) 212-214. https://doi.org/10.1016/0039-9140(72)80194-2
[7] C. Bravo-Díaz, E. González-Romero, A novel method for the determination of vitamin C in natural orange juices by electrochemical monitoring of dediazoniation of 3-methylbenzenediazonium tetrafluoroborate, *Analytica Chimica Acta* **385(1-3)** (1999) 373-384. https://doi.org/10.1016/S0003-2670(98)00727-2
[8] N. Matei, S. Birghila, V. Popescu, S. Dobrinas, A. Soceanu, C. Oprea, V. Magearu, Kinetic study of vitamin C degradation from pharmaceutical products, *Romanian Journal of Physics* **53(1-2)** (2008) 343-351. https://rjp.nipne.ro/2008_53_1-2/0343_0352.pdf
[9] S. M. Sultan, Y. A. Hassan, K. E. Ibrahim, Sequential injection technique for automated titration: Spectrophotometric assay of vitamin C in pharmaceutical products using cerium (IV) in sulfuric acid, *Analyst* **124** (1999) 917-921. https://doi.org/10.1039/A902000D
[10] M. A. Abdalla, H. M. Al-Swaidan, Iodimetric determination of iodate, bromate, hypochlorite, ascorbic acid and thiourea using flow injection amperometry, *Analyst* **114** (1989) 583-586. https://doi.org/10.1039/AN9891400583
[11] Y. Dilgin, G. Nişli, Fluorimetric determination of ascorbic acid in vitamin C tablets using Methylene Blue, *Chemical and Pharmaceutical Bulletin* **53(10)** (2005) 1251-1254. https://doi.org/10.1248/cpb.53.1251
[12] M. A. Memon, M. H. Memon, M.U . Dahot, I. A. Ansari, Spectrophotometric determination of ascorbic acid in pharmaceuticals by flow injection analysis using brown mono 1,10-phenaathroline-iron (III) complex as an oxidant, *Medical Journal of Islamic Academy of Sciences* **13(2)** (2000) 69-74. https://medicaljournal-ias.org/jvi.aspx/jvi.aspx? pdir=ias&plng=eng&un=IAS-74936
[13] S. P. Kounaves, *Voltammetric techniques handbook of instrumental techniques for analytical chemistry,* Tufts University, Department of Chemistry, Ch. 37, USA, 1997, p. 709. https://www.brown.edu/Departments/Engineering/Courses/En123/Lectures/potentiostat.pdf
[14] A. Sivanesan, P. Kannan, S. A. John, Electrocatalytic oxidation of ascorbic acid using a single layer of gold nanoparticles immobilized on 1,6-hexanedithiol modified gold electrode, *Electrochimica Acta* **52(28)** (2007) 8118-8124. https://doi.org/10.1016/j.electacta.2007.07.020
[15] P. Shakkthivel, S.-M. Chen, Simultaneous determination of ascorbic acid and dopamine in the presence of uric acid on ruthenium oxide modified electrode, *Biosensors and Bioelectronics* **22(8)** (2007) 1680-1687. https://doi.org/10.1016/j.bios.2006.07.026
[16] X. Zou, L. Luo, Y. Ding, Q. Wu, Chitosan incorporating cetyltrimethylammonium bromide modified glassy carbon electrode for simultaneous determination of ascorbic acid and dopamine, *Electroanalysis* **19(17)** (2007) 1840-1844. https://doi.org/10.1002/elan.200703945
[17] Y. Gao, H. Li, J. Tong, L. Wang, A new voltammetric sensor based on poly(Lcysteine)/GR composite film modified electrode for the sensitive determination of amaranth in wastewater, *Environmental Technology* **42(15)** (2021) 2385-2390. https://doi.org/10.1080/09593330.2019.1701569
[18] Ş. Z. B. Yağcı, Investigation of the voltammetric behaviors of some drug compounds at poly (p-aminobenzene sulfonic acid) electrode and quantitative determination in drug samples. *MSc Thesis*, İnönü University, Malatya, Turkey, 2011, 1-74. https://tez.yok.gov.tr/UlusalTezMerkezi/tezDetay.jsp?id=9dNAnzJlZyaHePjHTlfXEQ&no=JGj5SVaW8Nk4Kl3CkcnF9A
[19] T. Göver, Z. Yazıcıgil, Electrochemical study of 6-(ferrocenyl)hexanethiol on gold electrode surface in non-aqueous media, *Surfaces and Interfaces* **13** (2018) 163-167. https://doi.org/10.1016/j.surfin.2018.09.002

[20] T. Tabanlıgil Calam, E. Hasdemir, Comparative characterizations of self-assembled monolayers of 1, 6-hexanedithiol and 1-hexanethiol formed on polycrystalline gold electrode, *Comptes rendus de l'Acad´emie bulgare des Sciences* **72(3)** (2019) 316-326. https://www.researchgate.net/publication/332211482

[21] F. Tatli, D. Uzun, T. Tabanlıgil Calam, A. B. Gündüzalp, E. Hasdemir, Preparation and characterization of 3-[(1H-1, 2, 4-triazole-3-ylimino) methyl] naphtalene-2-ol film at the platinum surface for selective voltammetric determination of dopamine in the presence of uric acid and ascorbic acid, *Surface and Interface Analysis* **51(4)** (2019) 475-483. https://doi.org/10.1002/sia.6607

[22] T. Tabanlıgil Calam, The voltammetric determination of epinephrine on an Au electrode modified with electropolymerized 3,5-diamino-1,2,4-triazole film, *Gazi University Journal of Science C* **7(4)** (2019) 985-998. https://doi.org/10.29109/gujsc.623660

[23] Y. Öztekin, Z. Yazıcıgil, Preparation and characterization of a 1,10-phenanthroline-modified glassy carbon electrode, *Electrochimica Acta* **54(28)** (2009) 7294-7298. https://doi.org/10.1016/j.electacta.2009.07.050

[24] M. D. Rosso, C. H. Brodie, S. Ramalingam, D. M. Cabral, E. Pensini, A. Singh, C. M. Collier, Characterisation of graphene electrodes for microsystems and microfluidic devices, *Scientific Reports* **9** (2019) 5773. https://doi.org/10.1038/s41598-019-42108-x

[25] H. Liu, G. Wang, D. Chen, W. Zhang, C. Li, B. Fang, Fabrication of polythionine/NPAu/MWNTs modified electrode for simultaneous determination of adenine and guanine in DNA, *Sensors and Actuators B* **128(2)** (2008) 414-421. https://doi.org/10.1016/j.snb.2007.06.028

[26] Ş. Erogul, Preparation of electrochemical sensor based on Fe_3O_4 nanoparticle-graphene oxide for determination of catechol and hydroquinone. *MSc Thesis*, Selçuk University, Konya, Turkey, 2015, 1-78. https://tez.yok.gov.tr/UlusalTezMerkezi/tezDetay.jsp?id=G7LI0Hy0IJhopWy3iCfbGQ&no=xl1IxQ0Dt_z5uoG4jBjpIw

[27] P. Carro, G. Andreas, C. Vericat, M. E. Vela, R. C. Salvarezza, New aspects of the surface chemistry of sulfur on Au(111): Surface structures formed by gold-sulfur complexes, *Applied Surface Science* **487** (2019) 848-856. https://doi.org/10.1016/j.apsusc.2019.05.167

[28] F. Ağın, Voltammetric determination of guaifenesin on poly(Nile Blue) modified glassy carbon electrode in pharmaceutical dosage form, *Karadeniz Chemical Science and Technology* **2** (2018) 27-31. https://dergipark.org.tr/tr/download/article-file/498653

[29] D. He, P. Zhang, S. Li, H. Luo, A novel free-standing CVD graphene platform electrode modified with AuPt hybrid nanoparticles and L-cysteine for the selective determination of epinephrine, *Journal of Electroanalytical Chemistry* **823** (2018) 678-687. https://doi.org/10.1016/j.jelechem.2018.07.022