GLASSY CARBON ELECTRODE MODIFIED WITH GRAPHENE OXIDE AND GOLD NANOPARTICLES FOR ASCORBIC ACID DETECTION

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Abstract

Glassy carbon electrodes modified with graphene oxide (GO), gold nanoparticles (AuNP) and methylene blue (MB) were produced by drop casting method for ascorbic acid (AA) determination. Nafion was used as a polymeric immobilizing matrix.
The GCE/GO-AuNP-MB-Nafion and GCE/GO-AuNP-Nafion electrodes were characterized by using cyclic voltammetry and electrochemical impedance spectroscopy to investigate electrocatalytic effect, stability and reproductibility. After optimization, the analytical parameters of the modified electrodes were determined by amperometry. The limit of detection for ascorbic acid at GCE/GO-AuNP-Nafion modified electrode was 2.4 µM and the linear domain from 5 to 50 µM.
The electrodes showed significant electrocatalytic effect with good stability and reproductibility.

Introduction

Previous studies show, that glassy carbon electrodes have an anodic potential limit of approximately +1 V, depending on the electrolyte solution. Applying higher potentials will lead to polarization of the working electrode [1,2]. Thus, determining analytes with high oxidation potentials can lead to errors. This effect can be prevented by lowering oxidation potentials of analytes using modifying agents with electrocatalytic effect. Previously, graphene oxide, reduced graphene oxide and gold nanoparticles have been used as modifying agents with proven electrocatalytic effect [3,4,5,6].

L-ascorbic acid (vitamin C) is an important vitamin found in plants. It is an essential nutrient in human diet; insufficient levels of vitamin C can lead to the disease scurvy. It is also important in oxidative protection - being a potent antioxidant and reducing agent that functions in fighting bacterial infections - and in the formation of collagen for various tissues. L-ascorbic acid is widely available as a dietary supplement. Based on these, quantitative determination of ascorbic acid in biological and non-biological samples is of high importance [7]. Due to its relatively high oxidation potential (approximately 0.7 V, depending on the electrode used), analysis by electrochemical methods can be problematic and affected by interferences. For a reliable determination of ascorbic acid, lowering of the oxidation potential is needed.

In this context, our goal was to develop and optimize modified glassy carbon electrodes with a new synthesized graphene oxide (GO), gold nanoparticles (AuNP) and methylene blue (MB) using the drop-casting method for efficient ascorbic acid determination.

Immobilization of the modifying agents on the electrode surface can be achieved through a polymer matrix using Nafion or chitosan.

Experimental

The glassy carbon electrode surface was cleaned by polishing, using a 2.5 μm and a 0.3 μm particle size Al_2O_3 polishing powder from Buehler followed by three minutes of sonication in distilled water to clean it of any powder residue. The graphene oxide (GO) was prepared by dr. C. Cotet at the Faculty of Chemistry and Chemical Engineering by graphite exfoliation method [8], the Na_2HPO_4 2 H_2O, NaH_2PO_4 12 H_2O and a 5 w/w% Nafion in ethanol solution were supplied by Sigma Aldrich. The methylene blue was provided by Merck, 100% ethanol was provided by Reactivul Bucuresti, the 100% L-ascorbic acid was supplied by Madal Bal kft.

A 1 w/w% graphene oxide dispersion was prepared by sonication of the solid GO in distilled water for 5 hours and a further 30 minutes of mixing using a Vortex mixer. A sol of approximately 40 nm particle size gold nanoparticles was prepared using the Turkevich-Frens method. A 0.125 w/w% alcoholic Nafion solution was prepared by diluting the 5 w/w% solution. A 1 mM methylene blue solution was prepared by dissolving the powder in ethanol.
A 0.1 M phosphate buffer solution was prepared by dissolving appropriate amounts of Na_2HPO_4 and NaH_2PO_4 and adjusting the pH value to 7 with 0.1 M H_3PO_4 or NaOH solutions, respectively.

Modified glassy carbon electrodes have been produced by the drop-casting method. Mixtures of the prepared solutions have been sonicated for two minutes before drop casting on the glassy carbon electrode surface. Solvent evaporation was performed by air drying at room temperature for a minimum of 3 hours. The GO was then reduced by cyclic voltammetry during a pretreatment phase which consisted in potential cycling between -1 and 0 V.
Electrochemical measurements were using a PGSTAT-302 Autolab potentiostat (The Netherlands).
Optimization studies were performed using cyclic voltammetry, calibration curves were obtained using amperometry.

Results and discussion

Optimization studies have been conducted to determine the ideal amount of the modifying agents (GO, AuNP) and of the immobilizing agent (Nafion) in the presence of MB. Adding methylene blue did not yield the expected results and was kept constant (5 μL of 1 mM solution in ethanol) during the optimization procedure. Ideal results have been obtained by drop casting 2.5 μL of GO dispersion, 5 μL of AuNP sol and 3 μL of 0.125 % Nafion solution.

The oxidation potential of ascorbic acid at the bare glassy carbon and at GCE/GO-AuNP-Nafion modified electrode was 670 mV and 275 mV, respectively (Figure 1.). This shift of approximately 400 mV in oxidation potential suggests a strong electrocatalytic effect of the modifying agents.

A further study shows that the slope of the calibration curve for ascorbic acid determined using cyclic voltammetry has increased from 4.46 μA/mM in the case of the bare electrode to

6.06 μA/mM in the case of the GCE/GO-AuNP-Nafion modified electrode (results not shown).

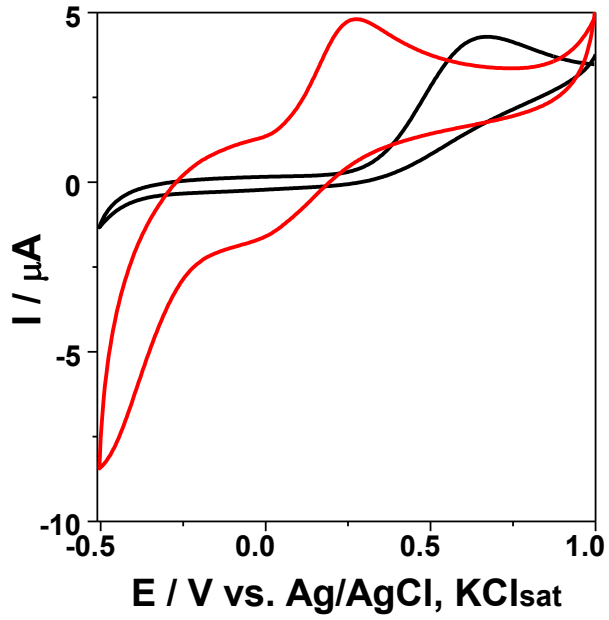

Figure 1. Cyclic voltammograms of 500 mM AA measured using a bare glassy carbon electrode (black) and a modified GCE/GO-AuNP-Nafion electrode (red).
Experimental conditions: electrolyte, phosphate buffer, pH 7; starting potential, +1 V *vs.* Ag/AgCl, KCl_{sat}.

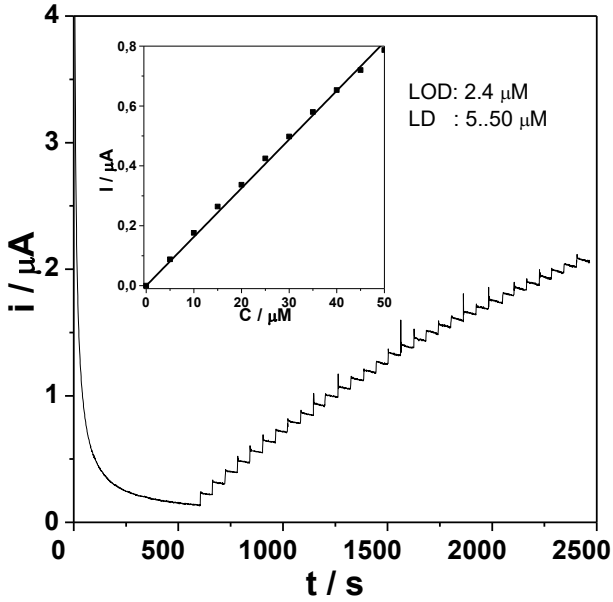

Figure 2. Amperometric measurement and calibration curve of AA using GCE/GO-AuNP-Nafion modified electrode.
Experimental conditions: electrolyte, phosphate buffer, pH 7; applied potential, +0.2 V *vs.* Ag/AgCl, KCl_{sat}, rotating speed, 500 rpm.

The amperometric calibration curve (Figure 2.) shows a good linear range measured up to 50 μM ascorbic acid (R^2 = 0.9994, no. of points = 11), with a low detection limit of 2.4 μM (signal/noise = 3).
EIS measurements show that impedance is increased by the immobilizing layer of Nafion and decreased by the GO and AuNPs (results not shown).

Conclusion

A novel, GCE/GO-AuNP-Nafion modified electrode for ascorbic acid detection has been produced, optimized and characterized. Using simple methods, we have managed to significantly decrease the oxidation potential and to increase peak height.
Further studies need to be made to determine short and long term stability and selectivity when measured in the presence of coexisting chemicals (interferents) with similar oxidation potentials, such as uric acid and dopamine.

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