Development of a porphyrazine – decorated nanoporous gold microsensor for ascorbate detection.

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Highlights

Gold microsensors were modified with nanoporous gold and cobalt (II) porphyrazine to detect ascorbate in natural orange samples by differential pulse voltammetry.

Resumo/Abstract

Ascorbate is a water-soluble vitamin with many functions. Among them, antioxidizing is one of the most important and known. In the immunologic system, ascorbate is a potent agent against free radicals produced endogenously and exogenously, and humans can get it by alimentation[1]. In this work, we show our efforts towards fabricating a cobalt (II) – porphyrazine/nanoporous gold sensor for ascorbate electrochemical detection. The microelectrode was lab-made using a 25 µm diameter gold fiber. The surface of the bare gold microelectrode sensor (µAu) was first activated through a dynamic hydrogen bubble template (DHBT)[2] method, and then modified with a cobalt-porphyrazine[3] compound. Briefly, a - 3.0 V potential was applied for 150 s in a 5 mmol L^{-1} $HAuCl_4$ + 0.5 mol L^{-1} H_2SO_4 solution. During this step, the chloroauric anion was reduced at the electrode surface simultaneously with the hydrogen bubble evolution, creating the nanoporous structure (NPG). Then, the NPG surface was modified by dip coating in a 100 µmol L^{-1} cobalt (II)-tetra(3,4-pyridyl)- porphyrazine (TRP) solution prepared in methanol. Compared to the µAu surface, the anodic oxidation of ascorbate exhibited a peak potential shift of about 850 mV to a less positive value using the NPG/TRP modified electrode, and a 100-fold current increase. Such a remarkable performance can be attributed to the synergic effect caused by the presence of numerous active sites in the NPG structure and the catalytic activity of the immobilized porphyrazine. Morphological and electrochemical characterizations were performed by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) techniques to evaluate the distribution of the catalyst particles in both sensors and to understand the mechanism involving the electron transfer step. An interference study was carried out, and a calibration curve was obtained along an extended ascorbate concentration range. The sensor will be applied as a miniaturized tool to get information on the role of ascorbate against cellular disorders caused by oxidative stress induced by UV irradiation in HaCaT cells (intra and extracellular).

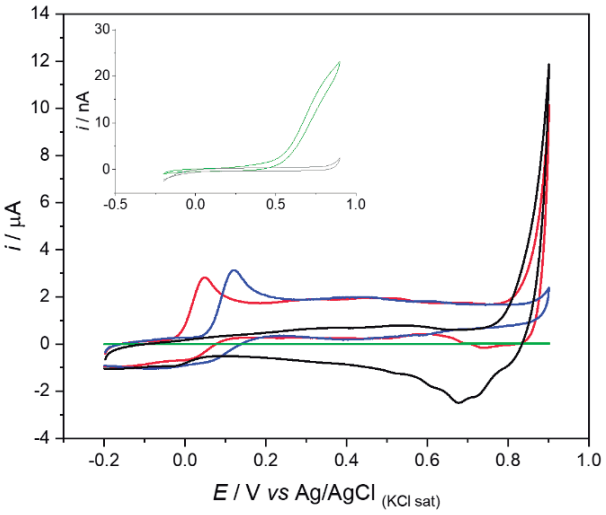

Figure 1 – Cyclic voltammograms (second cycle) recorded in phosphate buffer solution (pH ≈ 7) using a bare microelectrode (green curve) and the NPG-TRP modified microelectrode (black curve), and in phosphate buffer solution (pH ≈ 7) + 4 mmol L^{-1} AA with the NPG modified microelectrode (blue curve) and the NPG-TRP modified microelectrode (red curve). The inset shows a magnified CV recorded with the bare microelectrode in phosphate buffer solution (pH ≈ 7) + 4 mmol L^{-1} AA. Scan rate: 100 mV s^{-1}.

[1] Pisoschi, A. M.; Pop, A.; Serban, A. I.; Fafaneata, C.; *Electrochim. Acta* **2014**, *121*, 443.
[2] Regiart, M. et al. ; *ChemElectroChem* **2020**, *7*, 1558.
[3] Silva, H.N. et al. Molecules **2022**, 27, 4598.

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