



Screen-printed Organic Electrochemical Transistors for the detection of ascorbic acid in food



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ABSTRACT

Methods traditionally used for ascorbic acid (AA) detection in food are often expensive and complex, making them unsuitable for day-to-day determinations. In this work, we report on the use of all-PEDOT:PSS Organic Electrochemical Transistors (OECTs) for fast, simple and low-cost determination of AA in food. The performance of these OECTs was tested first with in lab-prepared solutions of AA with different concentrations. The effect of the geometry on the transistors performance for AA sensing was also investigated by comparing the response of two OECTs with different channel and gate areas ratio (γ), in terms of current modulation, sensitivity, background signal and limit of detection (LOD). OECTs with smaller gate electrode than the channel (large γ) show the best performance for AA sensing: these devices display smaller background signal, higher sensitivity, larger modulation and better LOD value (80 μ M). Since the AA content in food rich in Vitamin C is in the mM range, these transistors can be considered sensitive enough for quantitatively monitoring AA in food. In order to demonstrate the reliability of the proposed sensors in real food samples, the response of these transistors was additionally measured in a commercial orange juice. The amount of AA obtained with the OECTs is in good agreement with that determined by HPLC and with values reported in the literature for orange juices. Furthermore, these OECTs can be considered promising candidates for the selective detection of AA in the presence of other interfering antioxidants.

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1. Introduction

Ascorbic acid (AA), commonly known as Vitamin C, is a naturally occurring hydrosoluble organic compound that can be found in many biological systems and food products, namely fresh vegetables and fruits. In aqueous solution, AA shows two deprotonation steps (with pKa values of 4.17 and 11.57) [1]. Therefore, at typical biological pH values, AA occurs as monodeprotonated ascorbate anion. AA is known for its reductive properties, being easily oxidized to dehydroascorbic acid (DHAA) (Fig. 1). The oxidation of AA involves release of two electrons and two protons to produce DHAA [2]. Due to its strong antioxidant activity, AA is largely used as an antioxidant additive in food industry to prevent unwanted changes in color or flavor of food and drinks. Furthermore, the

content of Vitamin C is used as an index of the health-related quality of fruits and vegetables [3]. Consequently, there is increasing interest in the development of analytical methods for the quantitative determination of AA in food.

Traditional methods for the determination of AA in food include enzymatic techniques [4], liquid chromatography [5–7], spectrophotometry [8], chemiluminescence [9], capillary electrophoresis [10], and titration with an oxidant solution [11]. However, such detection methods often require expensive and complex instrumentation, making them unsuitable for day-to-day determinations. Therefore, the development of sensitive, simple, fast, and low cost techniques for the detection of AA is of great interest for food industry.

Electrochemical sensors can be a promising solution since they are based on the use of quick and easy procedures [2]. Among them, sensors based on organic semiconductor devices, like Organic Electrochemical Transistors (OECTs), can be regarded as a valid

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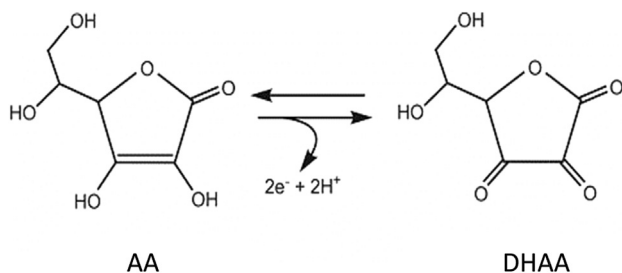
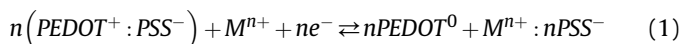


Fig. 1. Ascorbic acid (AA) and its two-electron oxidation product dehydroascorbic acid (DHAA) redox couple (redox potential $E_0 = +0.058$ V).

option for AA sensing. OECTs have attracted considerable interest in recent years for their application as chemical and biological sensors, due to their ability to operate in aqueous environments, easy fabrication, high sensitivity, and their simpler and cheaper readout electronics compared to conventional electrochemical sensors [12,13]. The essential components of an OECT are an organic semiconductor film, the channel (with source and drain electrodes), and an electrolyte bridging the channel and the gate electrode. As a convention, the source electrode is grounded and a voltage is applied to the drain electrode relative to ground. The operation of OECTs is based on the modulation of the channel current by electrochemical doping or de-doping from the electrolyte when gate voltages are applied.

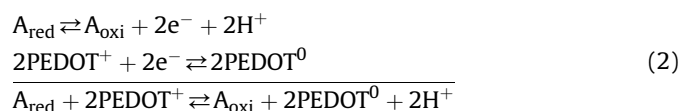
One of the most widely used conducting polymers in these devices is poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonate (PEDOT:PSS) [14,15]. PEDOT:PSS is commercially available and can be readily patterned by conventional photolithography [16,17], or by solution processing techniques like inkjet-printing [18,19] and screen-printing [20–22]. In addition, it exhibits high conductivity, excellent thermal stability and good stability in a wide pH range. Upon the application of a positive gate voltage in PEDOT:PSS-based OECTs, cations from the electrolyte migrate into the conducting polymer [23,24]. This in turn de-dopes PEDOT:PSS and leads to a decrease of the channel current. De-doping occurs by reduction of highly conducting PEDOT⁺ to less conducting PEDOT⁰, according to the following electrochemical reaction [25]:



where M^{n+} is a cation in the electrolyte, n is the number of charge of the cation and e^- is an electron from the source electrode. When the gate voltage is removed, cations migrate back into the electrolyte, and the original conductivity of the organic semiconductor is restored. As a result of this working principle, these devices have been successfully employed as chemical and biological sensors [24,26]. In OECTs based on PEDOT:PSS, the gate electrode [27], the device architecture (ratio between the channel and gate areas, channel geometry) [28,29], and the materials properties play an important role in the sensor performance.

PEDOT:PSS-based OECTs can operate either as ion-to-electron converters or as electrochemical sensors [29]. In OECTs that are used as *ion-to-electron converters*, a transient ionic current is converted into a change in the drain current. The application of a positive gate voltage causes an ionic current in the electrolyte. Cations from the electrolyte migrate into the conducting polymer and de-dope it, leading to the decrease of the drain current. It has been demonstrated that for operation as ion-to-electron converters, the use of a gate electrode that is much larger than the channel or a non-polarizable gate electrode improves the sensor performance [29].

In OECTs that are used as *electrochemical sensors*, charge transfer reactions between a species in the electrolyte and the gate electrode change the potential of the electrolyte, inducing a change in the drain current. For operation as electrochemical sensors, OECTs with gate electrode smaller than the channel exhibit higher sensitivity [29]. All-PEDOT:PSS OECTs can be used as electrochemical sensors for the determination of redox active species (like adrenaline, dopamine and AA) by exploiting the ability of this polymer to electrocatalytically oxidize such molecules at the gate electrode [21,30,31]. In particular, PEDOT can directly oxidize AA according to the following reaction scheme:



In addition, all-polymer sensors offer many advantages with respect to devices with metal gate electrode such as lower cost, easier fabrication and the possibility to be patterned in a flexible substrate.

In this communication, we report on the use of all-PEDOT:PSS OECTs as electrochemical sensors for the detection of AA in food. The performance of these OECTs was tested first with in lab-prepared solutions of AA with different concentrations. The effect of the geometry on the transistors performance for AA sensing was also investigated by comparing OECTs with different channel and gate areas ratio. Finally, the OECTs response was also measured in a commercial orange juice, in order to demonstrate the reliability of the proposed sensors in real food samples.

2. Materials and methods

2.1. Preparation of PBS solution

A 0.1 M Phosphate Buffered Saline (PBS) solution was prepared by dissolving K_2HPO_4 (Scharlau, Spain) and KH_2PO_4 (Scharlau, Spain) in Milli-Q water. The PBS solution had a pH of 4.8 as measured by pH meter.

2.2. Preparation of ascorbic acid solutions

Solutions were prepared by dissolving AA (Scharlau, Spain) in PBS solution with different molar concentrations (10^{-8} M, 10^{-7} M, 10^{-6} M, 10^{-5} M, 10^{-4} M, 10^{-3} M and 10^{-2} M).

2.3. Orange juice

Commercial ready-to-drink orange juice (Hacendado, Spain) purchased from a local supermarket was used as a model real sample. The selected product contains, according to the label, 48 mg/100 ml of Vitamin C. The juice was twice diluted with the PBS solution and used without further probe preparation.

2.4. Transistor fabrication

Commercially available PEDOT:PSS C2100629D1 (Gwent, UK) with 500–700 Ω /sq was used as the active material for the fabrication of the OECTs. The channel and the gate were obtained by screen-printing PEDOT:PSS over a polyester film. Screen-printing was performed with PET 1500165/420–34W/32 μ m mesh screen (Sefar, USA) and Dirasol 132 UV film (Fujifilm, USA). The final screen thickness was 55 μ m. UV light was used to transfer the OECT pattern to the screen. The PEDOT:PSS ink was re-dispersed for 1 h at 1000 rpm before printing. Printing was carried out using an Aurel

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