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Carbon black as successful screen-printed electrode modifier for phenolic compound detection

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ABSTRACT

We report a miniaturized and disposable electrochemical sensor for phenolic compound detection. The sensor was constructed by modifying the working electrode surface of screen-printed electrode (SPE) with carbon black (CB) dispersion. This new probe showed higher sensitivity and better resistance to fouling than the bare SPE, displaying the suitability of CB as an excellent nanomodifier of SPE for phenolic compound detection. Catechol, gallic acid, caffeic acid, and tyrosol were detected by square wave voltammetry with a detection limit of 0.1 μM, 1 μM, 0.8 μM, and 2 μM, respectively. The sensor was able to selectively discriminate the *mono*-phenols and *ortho*-diphenols with rapid and easy measurement, paving the way to use a cost-effective device for quality control of foods and beverages containing phenolic compounds.

1. Introduction

Polyphenolic compounds are common constituents of several foods and beverages and the major source of dietary antioxidants. The antioxidant activity is due to the presence of one or several phenolic groups, capable of reducing the toxic effect of reactive oxygen species and radical compounds. As antioxidants, the polyphenolic compounds are able to reduce several diseases associated to oxidative stress, including cardiovascular and neurodegenerative disorders [1]. Due to the versatile activity *in vivo* of these compounds, their detection is an important issue in analytical chemistry. The measurement is usually carried out using the Folin–Ciocalteu method, which involves the reduction of phosphomolybdic–phosphotungstic acid to form a blue colored complex [2]. The success of this colorimetric method, which is still largely used to assay total phenolic content of food, relies on the simplicity of the measurement and the low detection limit, usually in the mg/L range depending on the phenolic compound reactivity. However, this method lacks selectivity, it is not possible to discriminate between different compounds or classes of polyphenols. Sensitivity and selectivity can be largely improved by using methodologies such as liquid and gas chromatography, but the analysis cannot easily be performed on a routine basis [3,4]. Alternative methods for detection of phenolic compounds employ biosensing platforms with laccase or tyrosinase as biocomponent. The main advantages of biosensors are the small amount of compound necessary for the analyses as well as rapid measurement using miniaturized devices [5–7]. Nevertheless, they suffer from low selectivity and poor storage stability. In this context, electrochemical sensors represent a suitable alternative for rapid, reliable, cost-effective, and *in situ* analysis. Sensors using glassy carbon or carbon paste electrodes for direct electrochemical detection have been reported in literature [8,9], but with the main disadvantage of electrode fouling. To overcome this drawback, a valuable choice lies in the use of disposable screen-printed electrodes (SPEs), as reported by Capannesi et al. [10] and Enache et al. [11]. In the last decade, the use of bare SPEs has been widely replaced with SPEs modified with nanomaterials, such as gold nanoparticles, carbon nanotubes, and graphene, coupling the versatility of electrochemical devices with the well-known advantages of such materials [12–14].

In recent years, the carbonaceous nanomaterial carbon black (CB) became an interesting modifier of sensors, due to its excellent conductive and electrocatalytic properties, as well as its cost-effectiveness (about 1 euro/kg). The advantages of using CB for analyte detection have been demonstrated by our research group [15] and afterward, several research works have established its excellent electrocatalytic properties [16–24]. In this work, we report for the first time the analytical performances of SPEs modified with CB (CB-SPE) for the detection of several phenolic compounds.

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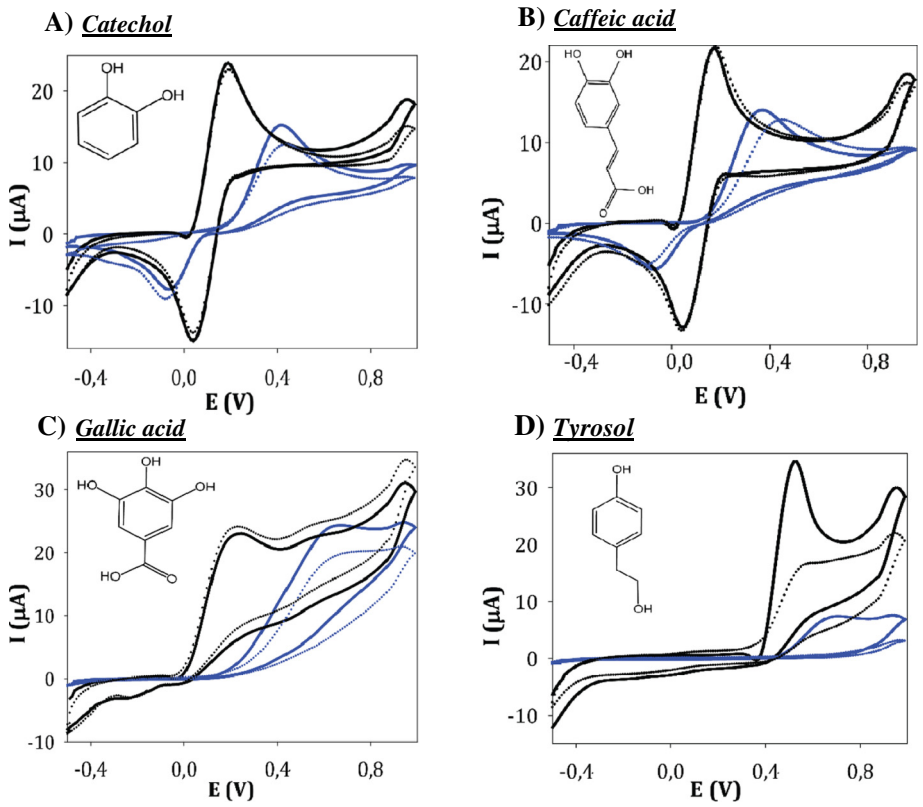

Fig. 1. CV using bare SPE (blue line) and CB-SPE (black line), scan rate 50 mV/s in phosphate-buffered solution 0.1 M + KCl 0.1 M, pH 7 in presence of catechol 1 mM (A), caffeic acid 1 mM (B), gallic acid 1 mM (C), and tyrosol 1 mM (D). First scan (continuous line) and fifth scan (dotted line).

2. Experimental

2.1. Apparatus and reagents

Cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were performed using a PalmSens portable instrument (the Netherlands). Commercial CB N220 was obtained from Cabot Corporation (Ravenna, Italy). All reagents used were of analytical grade and obtained from Sigma (St, Louis, MO).

2.2. Preparation of CB dispersion

CB powder was used to produce a dispersion in dimethylformamide (DMF):water (1:1) mixture at concentration of 1 mg/mL and then sonicated for 60 min at 59 kHz [18].

2.3. Preparation of CB-SPE

The screen-printed electrodes were produced in our laboratory with a 245 DEK (Weymouth, UK) screen-printing machine. The diameter of the working electrode was 0.3 cm resulting in a geometric area of 0.07 cm^2. The SPEs were then modified with CB via drop casting. A small volume (6 μL) of the CB dispersion was cast on the working electrode surface in three steps of 2 μL each.

3. Results and discussion

3.1. Cyclic voltammetry behavior of catechol, tyrosol, caffeic acid, and gallic acid at CB-SPE

The electrochemical behavior of CB-SPE toward several analytes such as NADH, ascorbic acid, and cysteine was reported in the literature [15,16,18], demonstrating improved electrochemical performances of CB-SPE not only in respect to bare SPE, but also in respect to SPE modified with graphene and carbon nanotubes [25]. To get a wide overview of CB electroanalytical performances, the electroanalytical response of CB-SPE toward some phenolic compounds was investigated. In the electrochemical detection of these compounds, one of the most relevant drawbacks is fouling of the working electrode, which is due to the adsorption of oxidation products to form a non-compact monolayer on the surface of the working electrode [26]. For this reason, the first part of this work was devoted to exploring the cyclic voltammetry behavior

Table 1
Analytical performances of SPE and CB-SPE. RSD% was calculated for analyte concentration of 30 μM (n = 3). LOD was calculated as signal to noise (S/N) = 3.

Analyte	Type of sensor	Equation	Sensitivity	R^2	Linear range (μM)	LOD (μM)	RSD%
Catechol	Bare SPE	$y = 0.0061x - 0.0015$	0.87 A M^{-1} cm^{-2}	0.960	5–50	3	9.0
	CB-SPE	$y = 0.126x - 0.019$	18 A M^{-1} cm^{-2}	0.999	1–50	0.1	3.6
Caffeic acid	Bare SPE	$y = 0.0054x - 0.0015$	0.77 A M^{-1} cm^{-2}	0.969	5–50	3	7.2
	CB-SPE	$y = 0.145x + 0.028$	20.7 A M^{-1} cm^{-2}	0.998	1–50	0.8	3.6
Gallic acid	Bare SPE	$y = 0.0025x + 0.001$	0.36 A M^{-1} cm^{-2}	0.903	10–100	3	8.5
	CB-SPE	$y = 0.0204x + 0.11$	2.91 A M^{-1} cm^{-2}	0.982	10–100	1	7.4
Tyrosol	CB-SPE	$y = 0.0167x + 0.0207$	2.38 A M^{-1} cm^{-2}	0.995	10–100	2	2.2