



Electrochemical sensor for amino acids and glucose based on glassy carbon electrodes modified with multi-walled carbon nanotubes and copper microparticles dispersed in polyethylenimine



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ABSTRACT

This work reports the analytical performance of glassy carbon electrodes (GCE) modified with multi-walled carbon nanotubes (CNT) and copper microparticles dispersed in polyethylenimine (PEI) (GCE/CNT-PEI-Cu) for the quantification of amino acids, albumin and glucose. The best analytical performance was obtained with CNT-PEI-Cu prepared by sonicating for 15.0 min a mixture of 1.0 mg mL⁻¹ PEI, 1.0 mg mL⁻¹ CNT and 3.0 mg mL⁻¹ copper microparticles. In the case of amino acids and albumin, the analytical signals were obtained from the increase of the copper oxidation signal produced as a consequence of the complex formation between Cu(II) and the amino acids. The sensor allowed the highly sensitive (submicromolar levels) and reproducible (3.9%) amperometric quantification of histidine, serine and cysteine at very low potentials (0.000 V) and pH 7.40. Albumin was quantified by Square Wave Voltammetry after 10.0 min interaction at -0.100 V with detection limits of 1.2 mg mL⁻¹.

GCE/CNT-PEI-Cu was also used for the quantification of glucose by amperometry at 0.700 V in a 0.100 M sodium hydroxide solution through the known catalytic activity of copper towards the oxidation of glucose, with highly competitive detection limits (182 nM). GCE/CNT-PEI-Cu was successfully used for the quantification of amino acids and albumin in pharmaceutical products and carbohydrates in beverages.

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1. Introduction

Electrochemical (bio)sensors have received considerable attention in the last years due to their known advantages such as low cost, high sensitivity, versatility, simplicity, and portability [1]. Since 1996 [2], we have witnessed an explosive growth of carbon nanotube (CNT)-based electrochemical (bio)sensors mainly due to the unique properties of this nanomaterial [3,4], especially those connected with electrochemistry like the strong electrocatalytic activity, the large decrease of surface fouling and the noticeable increase of the electroactive area [3, 5,6].

The incorporation of CNTs in biosensors requires minimizing their trend to aggregation. To overcome this inconvenience CNTs have been dispersed in solvents [7], ionic liquids [8] and polymers [9–18]. Particularly, polyethylenimine (PEI) has demonstrated to be highly efficient to disperse CNTs [9]. Glassy carbon electrodes (GCE) modified with MWCNT-PEI dispersions have been successfully used for the quantification of dopamine in the presence of ascorbic acid and serotonin [19], phenols [20], and herbicides like amitrol [20]. PEI-CNT modified

GCE has been also used for the adsorption of oligo and polynucleotides [21].

This work is focused on the development of an electrochemical sensor for the quantification of amino acids and glucose based on the modification of GCE with a dispersion of multi-walled carbon nanotubes (MWCNT), copper microparticles and PEI (GCE/CNT-PEI-Cu).

The quantification of amino acids using electrochemical sensors has been based on the direct electrooxidation of tyrosine, tryptophan and cysteine [22,23], or the catalytic oxidation in 0.10 M NaOH at Cu [24], Ni [25] or carbon electrodes modified with these metals [26,27]. Luque et al. [28] have reported the sensitive quantification of amino acids and albumin using carbon nanotube paste electrodes (CNTPE) modified with copper microparticles through the facilitated dissolution of copper in the presence of the amino acids. The direct quantification of electroactive amino acids in strong alkaline medium using copper electrodes in connection with HPLC has been also reported [29].

The non-enzymatic quantification of carbohydrates has been mainly based on the use of spectroscopic techniques with a previous step of derivatization [30]. The direct electrooxidation at platinum and gold electrodes has been also used; nevertheless, the procedure requires a continuously pulsed program to reduce the surface fouling [31]. In the last years, CNTs modified with metallic particles like CuO, Pt or copper

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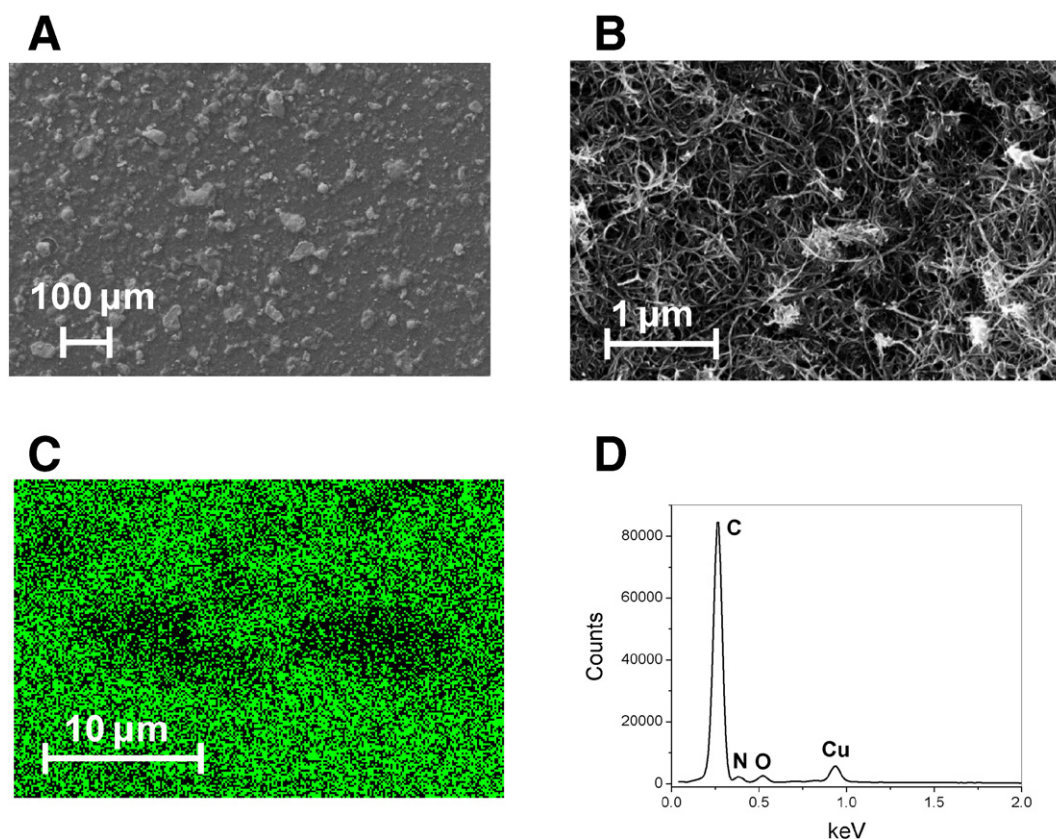


Fig. 1. FE-SEM pictures for CNT-PEI-Cu obtained with different magnifications: (A) 70 \times and (B) 18k \times . (C) EDX mapping for CNT-PEI-Cu, magnification: 10k \times ; (D) EDX spectrum of CNT-PEI-Cu.

nanoclusters have been also proposed for the direct electrochemical quantification of glucose [32–35].

In the following sections, we discuss the more relevant aspects about the characterization of GCE/CNT-PEI-Cu using Scanning Electron Microscopy (SEM), X-Ray Dispersion Energy (EDX), amperometry and cyclic voltammetry, and the analytical performance of the resulting electrodes for the quantification of amino acids, albumin and glucose.

2. Experimental

2.1. Reagents

Polyethylenimine (PEI, average MW 750,000, catalog number P-3143), bovine serum albumin (Alb, A-4503), L-cysteine, L-histidine, and L-serine were purchased from Sigma. Copper microparticles (99% purity, -325 mesh, 10% max, +325 mesh, 99%) were acquired from Alfa-Aesar. Multiwalled carbon nanotube powder (MWCNT) (diameter (30 ± 15) nm, length 1–5 μ m and >95% of purity) was obtained from NanoLab (U.S.A.). Glucose and sodium hydroxide were from Merck. Human serum albumin 20% intravenous injection was received from “Laboratorio de hemoderivados”, UNC (Córdoba, Argentina) while L-cysteine capsules (Tricomax 2) were obtained from Cassara Laboratory. The beverages were purchased in a local supermarket.

Amino acids stock solutions were daily prepared using a 0.050 M phosphate buffer solution pH 7.40 as supporting electrolyte. All solutions were prepared with ultrapure water ($\rho = 18 \text{ M } \Omega \text{ cm}$) from a Millipore-MilliQ system.

2.2. Apparatus

The measurements were performed with EPSILON (BAS) and TEQ_04 potentiostats. The electrodes were inserted into the cell (BAS,

Model MF-1084) through holes in its Teflon cover. A platinum wire and Ag/AgCl, 3 M NaCl (BAS, Model RE-5B) were used as counter and reference electrodes, respectively. All potentials are referred to the latter. A magnetic stirrer provided the convective transport during the amperometric measurements. Scanning Electron Microscopy (FE-SEM) images were obtained with a Field Emission Gun Scanning Electron Microscopy (FE-SEM Zeiss, SIGMA model). EDX mapping was obtained

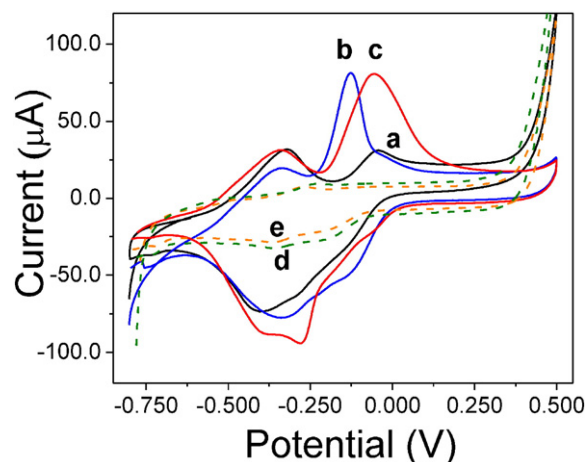


Fig. 2. Cyclic voltammograms obtained at GCE/CNT-PEI-Cu in a 0.050 M phosphate buffer solution pH 7.40 (a, —) and in a 0.050 M phosphate buffer solution pH 7.40 containing 5.0×10^{-4} M histidine (b, —) and 5.0×10^{-4} M L-serine (c, —). The corresponding voltammograms obtained at GCE/CNT-PEI in a 0.050 M phosphate buffer solution pH 7.40 containing 5.0×10^{-4} M histidine (d, - -) and 5.0×10^{-4} M L-serine (e, - -) are also included. Scan rate: 0.100 V/s.

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