



New electrode architectures based on poly(methylene green) and functionalized carbon nanotubes: Characterization and application to detection of acetaminophen and pyridoxine



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ABSTRACT

New electrode platforms have been constructed containing the redox polymer poly(methylene green) (PMG) and functionalized carbon nanotubes (*f*CNT) in two configurations, the first containing MG electropolymerised on a graphite composite electrode (CE) and covered with *f*CNT (*f*CNT/PMG/CE), the second having the MG electropolymerised on top of *f*CNT modified CE (PMG/*f*CNT/CE). Modified electrodes with both configurations were characterized by cyclic voltammetry and electrochemical impedance spectroscopy, and compared with PMG/CE and *f*CNT/CE and CE, in order to evaluate the role of each component in the modified electrode architecture. The modified electrodes were applied to the detection of acetaminophen and pyridoxine, by fixed potential amperometry and differential pulse voltammetry, the latter allowing the simultaneous detection of both analytes. The analytical properties of *f*CNT/PMG/CE and PMG/*f*CNT/CE sensors were obtained and the best analytical performance compared with recently reported acetaminophen and pyridoxine sensors. Determination of both analytes in pharmaceutical samples was successfully performed.

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1. Introduction

Electroactive polymers comprise a relatively new class of organic materials, which exhibit both electronic and ionic conductivity. The best way to prepare films of electroactive polymer is by electropolymerisation of the redox-active monomer, as is the case of phenazine monomers [1]. Electropolymerised films of phenazines have been extensively used in electrochemical sensors and biosensors [2], poly(methylene green) (PMG) being mostly utilized for electrocatalysis of NAD⁺ regeneration [3–5], and consequently for the development of biofuel cells based on NAD⁺-dependent dehydrogenase enzymes [6–11]. PMG's catalytic activity can be attributed to its structure, being similar to flavonoids, natural antioxidants responsible for many catalytic oxidation in nature [12], and because its half wave potential is more positive than that of NADH [11].

Carbon nanotubes (CNT) are now widely known as excellent materials for the construction of electrochemical sensors leading to improved analytical properties, compared with many other

carbon materials, such as higher sensitivity, lower limit of detection, due to their enhanced electronic properties, a large edge plane/basal plane ratio, and faster electrode kinetics [13]. CNT have been also used together with PMG, synergetic effects having been demonstrated in dehydrogenase-based reagentless biosensors [14], in a malate dehydrogenase “bucky” paper anode [6], in ethanol/air biofuel cells [9], and in a glucose dehydrogenase based bioanode [9].

The present work focuses on the development and characterization of new electrode architectures based on the redox polymer poly(methylene green) and functionalized CNT (*f*CNT) on graphite-epoxy composite electrode (CE) substrates, containing PMG covered with *f*CNT (*f*CNT/PMG/CE), or with PMG on top of *f*CNT (PMG/*f*CNT/CE). Epoxy composite electrodes have been previously used successfully as electrode substrates in many applications e.g. [15–17]. CNT were first functionalized in nitric acid, to increase their hydrophilicity and introduce functional groups [18], and then dispersed in a chitosan matrix, a biopolymer with good adhesion on solid substrates, high water and anion/cation permeability, high mechanical strength and excellent film-forming ability [19]. The modified electrodes were characterized by cyclic voltammetry and electrochemical impedance spectroscopy (EIS), and then applied to the determination of acetaminophen and pyridoxine,

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exploring the benefits of modification by both *f*CNT and PMG. Acetaminophen (paracetamol, N-acetyl-p-aminophenol), is a widely used analgesic anti-pyretic drug, [20], its electrochemical detection using CNT being successfully demonstrated e.g. [21], and it was determined here by differential pulse voltammetry (DPV) and fixed potential amperometry. Pyridoxine, one of the compounds of the vitamin B6 group, was also electrochemically determined; several methods exist for the determination of vitamin B6 in pharmaceutical formulations [22], electrochemical ones also having been reported [23–26].

2. Experimental

2.1. Reagents and solutions

All reagents were of analytical grade and were used without further purification. Millipore Milli-Q nanopure water (resistivity $\geq 18 \text{ M}\Omega \text{ cm}$) was used for the preparation of all solutions.

Methylene green, potassium hexacyanoferrate(II), potassium nitrate were from Fluka, chitosan (low molecular weight), sodium and potassium chloride, acetaminophen (ACOP), pyridoxine, monobasic and dibasic sodium phosphate were from Sigma and sodium tetraborate from May & Baker.

Polymerization of MG was carried out in a solution containing 1.0 mM MG dissolved in 0.025 M $\text{Na}_2\text{B}_4\text{O}_7 + 0.1 \text{ M KNO}_3$, pH 9.2.

The determination of acetaminophen and pyridoxine was done in sodium phosphate buffer saline 0.1 M NaPBS, containing 0.1 M $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 + 0.05 \text{ M NaCl}$, pH 7.0.

2.2. Instrumentation

Electrochemical experiments were performed in a three electrode cell, containing the composite electrode (CE) (area 0.126 cm^2) as working electrode, a Pt wire counter electrode and an SCE reference electrode, using a potentiostat/galvanostat μ -Autolab system (Metrohm-Autolab, Netherlands).

EIS experiments were carried out by using a PC-controlled Solartron 1250 Frequency Response Analyzer, coupled to a Solartron 1286 Electrochemical Interface using ZPlot 2.4 software (Solartron Analytical, UK), with an rms perturbation of 10 mV applied over the frequency range 65.5 kHz–0.1 Hz, with 10 frequency values per frequency decade.

The pH measurements were carried out with a CRISON 2001 micro pH-meter (Crison Instruments SA, Barcelona, Spain).

All experiments were carried out a room temperature ($25 \pm 1 \text{ }^\circ\text{C}$).

2.3. Preparation of modified graphite-epoxy composite electrodes

Graphite-epoxy electrodes were prepared using graphite powder and Araldit epoxy resin/hardener as described previously [27]. Before each use, the surface of the composite electrode was wetted with Milli-Q water and then thoroughly smoothed, first with abrasive paper and then with polishing paper, (Kemet, UK).

Multi-walled CNT (MWCNT) were purified and functionalized as described elsewhere [28]. First, a dispersion of CNT in 3 M nitric acid solution was stirred for 20 h, the solid product was collected on a filter paper and washed until the filtrate solution became neutral. The *f*CNT obtained were then dried in an oven at $80 \text{ }^\circ\text{C}$ for 24 h. A dispersion of 1% *f*CNT was prepared in 1.0% m/m chitosan (Chit) dissolved in 1.0% v/v acetic acid. A volume of $10 \mu\text{l}$ of this dispersion was dropped two times on the surface of CE or PMG/CE, leaving to dry each time for $\sim 60 \text{ min}$.

MG was electropolymerised on CE or on *f*CNT/CE from 1.0 mM MG dissolved in 0.025 M $\text{Na}_2\text{B}_4\text{O}_7 + 0.1 \text{ M KNO}_3$, pH 9.2 by cycling

the potential at 50 mV s^{-1} , for 40 cycles, between -0.5 and $+1.0 \text{ V}$ vs. SCE, for the CE, and between -0.6 and $+1.0 \text{ V}$ vs. SCE for *f*CNT/CE [29]. The electrodes were left to dry for at least 24 h before use.

2.4. Sample preparation

Acetaminophen and pyridoxine tablets were first finely ground in a mortar and then an appropriate amount was weighed and dissolved in 0.1 M NaPBS buffer to form 66.0 mM and 29.6 mM acetaminophen and pyridoxine solutions, respectively.

3. Results and discussion

3.1. Electropolymerization of MG on CE and *f*CNT/CE and CV characterization of *f*CNT/PMG/CE and PMG/*f*CNT/CE

PMG polymer was deposited on CE and *f*CNT/CE by potential cycling, in a solution containing MG monomer; CVs recorded during polymerization are displayed in Fig. 1. Polymerization begins with the formation of cation radicals at potentials close to $+1.0 \text{ V}$ vs. SCE, similar to other phenazine monomers [2]. On both substrates, CE and *f*CNT/CE, there is increase in oxidation/reduction polymer peak currents with each polymerization cycle, the potentials of which coincide with the monomer peaks. On *f*CNT/CE (Fig. 1b) the currents are significantly higher, due to the higher surface area of *f*CNTs and the polymer is better formed, the

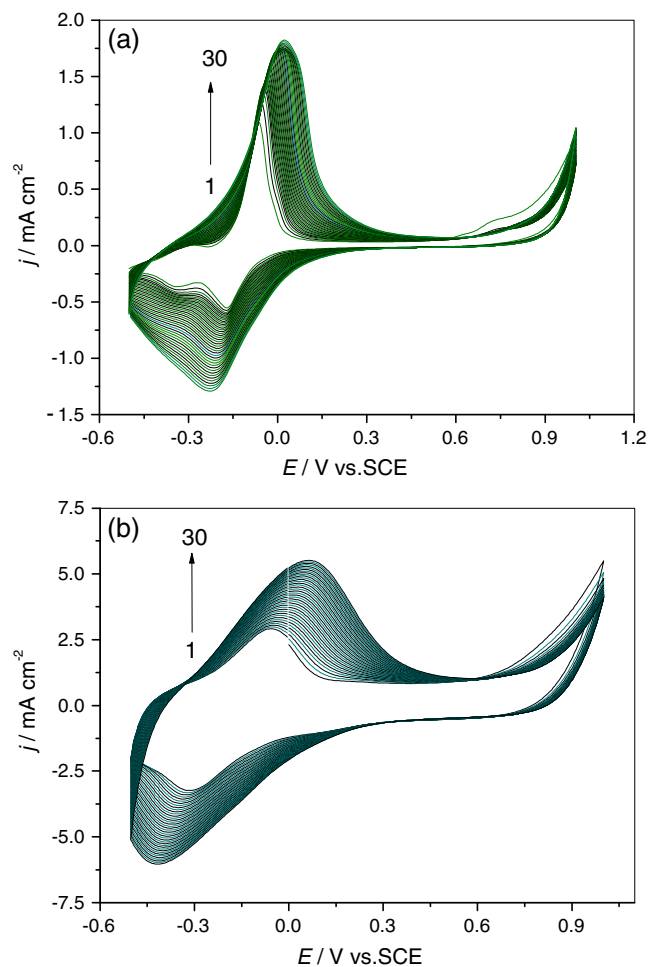


Fig. 1. CV-s recorded during the polymerization of MG on (a) CE and (b) *f*CNT/CE from a solution containing 1 mM MG in 0.025 M $\text{Na}_2\text{B}_4\text{O}_7 + 0.1 \text{ M KNO}_3$, pH 9.25; $\nu = 50 \text{ mV s}^{-1}$.

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