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ORIGINAL PAPER

Poly(brilliant green)/carbon nanotube-modified carbon film electrodes and application as sensors

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Abstract Poly(brilliant green) (PBG) films were formed on carbon film electrodes (CFE) by electropolymerisation of brilliant green monomer using potential cycling or at fixed potential from different pH solutions. The modified electrodes, PBG/CFE, were characterised by cyclic voltammetry (CV) in electrolytes of different pH by electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). In order to increase the stability of the polymer film and enhance the response, multi-walled carbon nanotubes (MWCNTs) were first deposited on CFE and then PBG was formed on top, PBG/CNT/CFE. The modified electrodes were applied to the amperometric determination of ascorbic acid (AA) in phosphate buffer pH7.0 at 0.0 V vs. saturated calomel electrode (SCE) and the results were compared, the presence of CNT leading to a significant increase in sensitivity. An interference study was carried out and good separation between AA and dopamine (DA) peaks was achieved that led to the successful determination of DA without interferences. Other interferents: aspirin, acetaminophen, salicylic acid and uric acid exhibited no response on the PBG/CNT/CFE. Determination of AA in pharmaceutical samples was successfully performed.

Keywords Brilliant green · Carbon film electrodes · Ascorbic acid · Carbon nanotubes · Dopamine

Introduction

The electrochemical properties of electroactive phenazine polymers make them highly suitable for preparation of modified electrodes, with investigation continuing into their synthesis and characterisation, properties and applications [1–7]. Electropolymerisation of monomers is very attractive, since the operational stability of the polymer film is increased compared with the adsorbed monomers and it is also easier to control film thickness by adjusting experimental parameters.

Brilliant green (BG) is a triarylmethane dye (Scheme 1a), similar to malachite green (MG) and is also known as MG G. The voltammetric response of MG has been studied [8] and several modified electrodes, mainly glassy carbon modified with poly(MG) by electropolymerisation, have already been reported as well as some applications [3, 9–14]. However, to our knowledge, there are no reports for poly(brilliant green) (PBG) synthesis, characterisation and application in the literature.

Carbon nanotubes (CNTs) represent an important group of nanoscale materials with interesting electrocatalytic properties besides high surface area per volume. Their electro-activity is attributed to the presence of reactive groups on the surface, the electrocatalytic effects being associated with structural defects [15, 16]. Thus, in general, a lower over-potential and higher peak currents are observed in the voltammetric response at electrodes modified with CNTs [17–19]. Due to these unique properties, CNTs have received enormous attention for the preparation of electrochemical sensors [20, 21] that has been amply reviewed [22–24].

This work focuses on the development, characterisation and application of novel PBG and PBG/CNT-modified

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carbon film electrodes (CFE), reported for the first time. Electropolymerisation was performed either by potential cycling or potentiostatically, at fixed potential, in buffer solutions with different pH values. Characterisation of the PBG films was carried out by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). In order to improve stability of the PBG film, modified electrodes were prepared in which multi-walled CNTs were first cast on the CFE and afterwards, BG was polymerised. The PBG/CFE- and PBG/CNT/CFE-modified electrodes were applied as sensors for ascorbate, possible interferences were assessed and comparison of analytical parameters made with literature data. Detection of dopamine (DA) by differential pulse voltammetry (DPV) was also performed.

Experimental

Reagents and solutions

All reagents were of analytical grade and were used without further purification. Brilliant green (BG) was from Fluka and L-ascorbic acid (AA) was from Sigma-Aldrich. Multi-walled CNTs (MWCNTs) were from NanoLab, USA, with ~95 % purity, 30±10 nm diameter and 1–5 μm length. Chitosan (Chit) of low molecular weight with a degree of deacetylation of 80 % was obtained from Sigma-Aldrich. DA hydrochloride and acetaminophen were from Sigma-Aldrich.

All solutions were prepared using Millipore Milli-Q nanopure water (resistivity>18 MΩcm. The supporting electrolyte for sensor evaluation was sodium phosphate buffered saline (NaPBS) (0.1 M NaH_2PO_4/Na_2HPO_4+ 0.05 M NaCl), pH7.0. For BG electropolymerisation, 0.1 M sulphuric acid pH1.0 and McIlvaine's universal buffer (0.1 M citric acid+0.2 M Na_2HPO_4) with pH values between 2.0 and 7.0 were used.

Methods, instruments and cell

All measurements were performed in a 15 mL, one-compartment cell containing a modified CFE as working electrode, a platinum wire auxiliary electrode and a saturated calomel electrode (SCE) as reference. Voltammetric and amperometric experiments were carried out using a CV-50 W Voltammetric Analyser from Bioanalytical Systems, controlled by BAS CV-2.1 software. A PalmSens potentiostat (Palm Instruments BV) was also used.

EIS measurements were performed using a Solartron 1250 Frequency Response Analyser, coupled to a Solartron 1286 Electrochemical Interface controlled by ZPlot software. The frequency range used was 65 kHz to 0.1 Hz with 10 frequencies per decade and integration time 60 s, with an rms perturbation voltage of 10 mV. Fitting to equivalent circuits was performed with ZView 3.1 software.

SEM images were obtained using a Jeol JSM 5310 scanning electron microscope. Indium tin oxide (ITO) electrodes were used as substrate and modification was done in the same way as on CFE (see next section). pH measurements were performed with a Crison 2001 micro pH meter. All experiments were performed at room temperature, 25±1 °C.

Carbon film electrode preparation and modification

The working electrodes were made from carbon film resistors (2Ω nominal resistance, 15 μm film thickness) of length 6 mm and 1.5 mm diameter. The resistors were fabricated from ceramic cylinders by pyrolytic deposition of carbon from methane in nitrogen atmosphere [25]. One of the two tight-fitting metal caps, linked to an external contact wire, was removed and the other one covered in plastic and protected by normal epoxy resin. The geometric area of the electrodes is 0.20 cm^2.

Since CFE surfaces cannot be renewed by polishing or other mechanical methods, electrochemical pre-treatment was always performed before electrode use to achieve a reproducible electrode response. This consisted of cycling the potential between −1.0 and +1.0 V vs. SCE at 100 mV s^{-1} until a stable voltammogram was obtained.

Carbon nanotube functionalisation and deposition

MWCNTs were purified and functionalised as described elsewhere [26]. A mass of 120 mg of MWCNT was stirred in 10 mL of a 5 M nitric acid solution for 24 h in order to cause partial destruction of the CNTs and introduce –COOH groups at the ends and sidewall defects of the CNTs. The solid product was collected on a filter paper and washed several times with nanopure water until the filtrate solution became neutral (pH≅5). The functionalised MWCNT were then dried in an oven at 80 °C for 24 h.

In order to prepare a 1.0 %w/v Chit solution, 100 mg of Chit powder was dissolved in 10 mL of 1.0 %v/v acetic acid solution and stirred for 3 h at room temperature to ensure complete dissolution. The Chit solution was stored at 4 °C.

A 1.0 %w/v MWCNT solution was prepared by dispersing 3 mg of functionalised MWCNTs in 300 μL of 1.0 % w/v Chit in 1.0 %v/v acetic acid solution and sonicating for 2 h. For CNTs, deposition a 10 μL drop of the 1 %w/v MWCNT solution in 1.0 %w/v Chit was placed on the surface of the CF electrode, left to dry in air at room temperature and this step was then repeated.

Brilliant green polymerisation

PBG films were obtained by electropolymerisation using either potentiostatic or potentiodynamic techniques. Prior to polymerisation, the electrode was activated as described in Ref. [14] for MG by cycling in 0.1 M sulphuric acid between −1.0 and +2.0 V at 100 mVs^{-1} until a stable voltammogram was obtained. Polymerisation was carried out in an aqueous solution containing 1 mM brilliant green in 0.1 M sulphuric acid or McIlvaine's buffer with different pH values. For potential cycling polymerisation, the electrodes were swept between −1.0 and +1.2 V at a scan rate of 100 mVs^{-1} during 10 cycles. Potentiostatically, a fixed potential of +1.2 V was applied during 440 s. The electrodes modified with PBG on CFEs are designated PBG/CFE and those where PBG was deposited onto CNT-modified electrodes, PBG/CNT/CFE.

Ascorbate sample preparation

Aspirin and paracetamol tablets, both with vitamin C, containing 240 mg and 250 mg AA, respectively, were purchased from a local pharmacy. Before testing, tablets were dissolved in 100 mL Milli-Q water.

Results and discussion

Polymerisation of brilliant green

PBG was formed on CFEs, PBG/CFE, or MWCNT-modified CFEs, PBG/CNT/CFE. The potentiodynamic and potentiostatic electropolymerisation conditions were optimised on CFE in different pH electrolytes and with different monomer concentrations.

Since no reports on brilliant green electropolymerisation were found, the deposition of PBG was performed as described for poly(MG) due to the similar structure of the monomers. Prior to polymerisation, the electrode was activated as described in Ref. [14] for MG deposition at glassy carbon as detailed in “Brilliant green polymerisation” This procedure increases electrode activity, which was confirmed by an increased rate of PBG formation.

Electropolymerisation was carried out in an aqueous solution containing 1 mM brilliant green in 0.1 M sulphuric acid or McIlvaine's buffer with different pH values, between 2.0 and 6.0. For potential cycling, the potential was swept between −1.0 and +1.2 V at a scan rate of 100 mVs^{-1} during 10 cycles. For fixed potential polymerisation, +1.2 V vs. SCE was applied during 440 s: the potential and time were chosen from CV data in order to get films similar to those obtained after 10 potential cycles as well as an applied potential positive enough to achieve oxidation of the monomer necessary for initiation, whilst avoiding over-oxidation.

Cyclic voltammograms for PBG deposition from a solution of 0.1 M sulphuric acid, pH 1.0 are shown in Fig. 1a and from McIlvaine's buffer, pH 4.0, in Fig. 1b. In both cases, there is a pH-dependent irreversible oxidation peak B: 0.82 V (pH 1.0) and ~0.98 V (pH 4.0), which corresponds

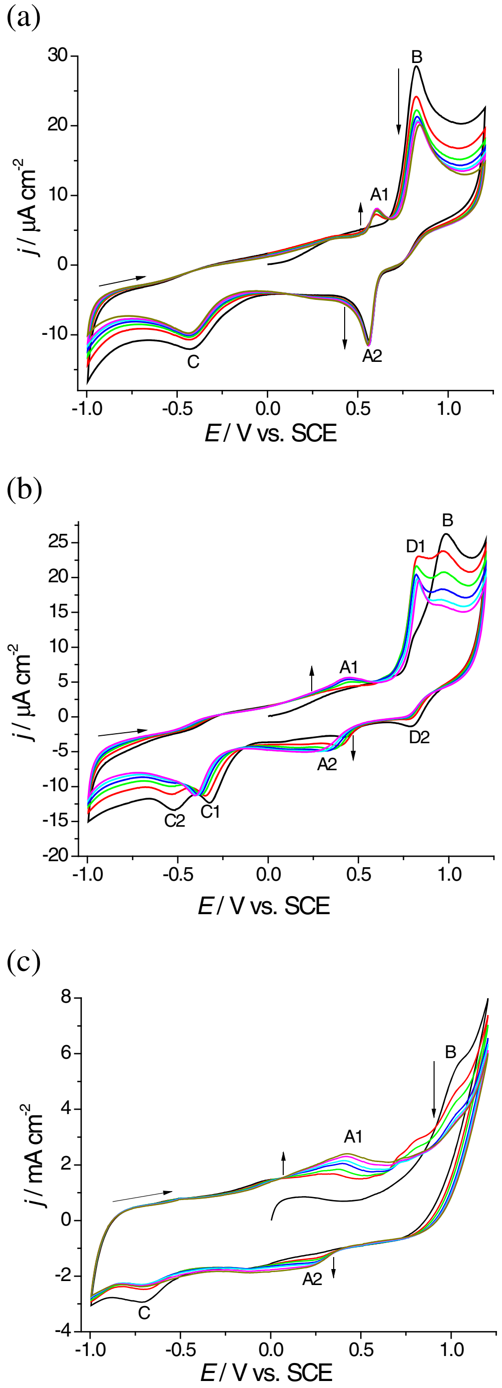


Fig. 1 Cyclic voltammetry for polymerisation of 1 mM BG between −1.0 and 1.2 V at 100 mVs^{-1} **a** 0.1 M sulphuric acid, **b** and **c** McIlvaine’s buffer pH4.0; at **a** and **b** CFE and **c** CNT/CFE

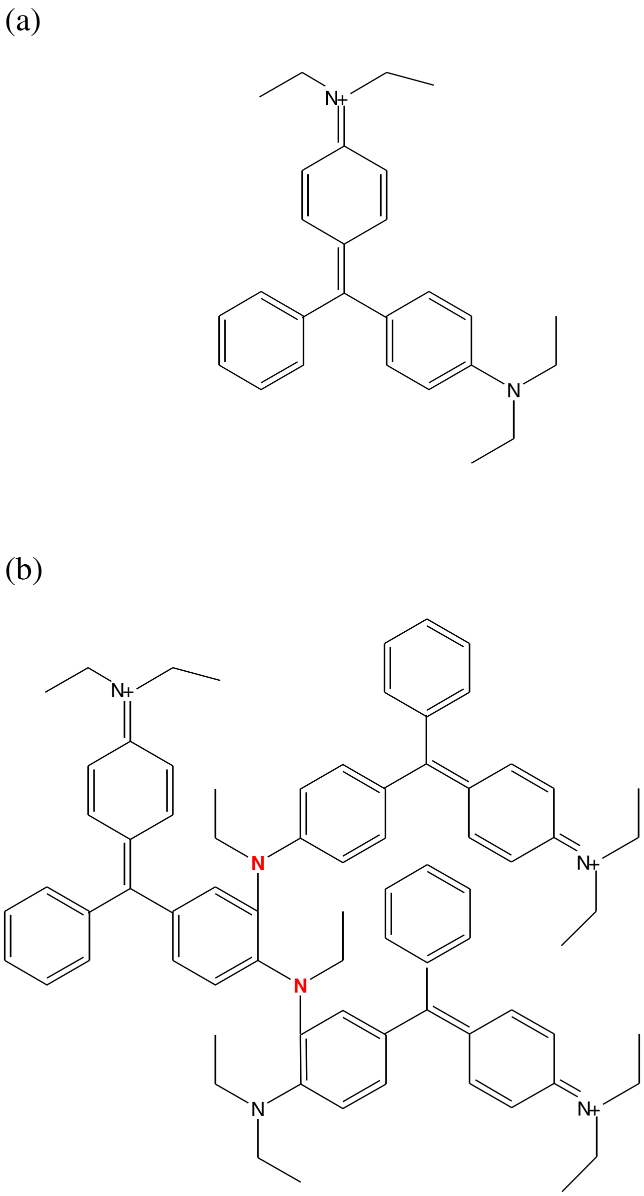
to monomer oxidation to the cation radical responsible for polymer initiation, similar to other dyes [2, 4, 27]. This current peak decreases in size with each cycle. In pH4.0 McIlvaine's buffer solution, another pair of peaks appears (D1 and D2) at 0.83 and 0.79 V, respectively. Peak D2 decreases with each cycle, at the end of the polymerisation just appearing as a shoulder, this shoulder also being observed in pH1.0 solution. The height of peak D1 at pH4.0 increases with each cycle. Peaks B and D1 can be ascribed to intermediate forms of partially oxidised monomer, which are probably not very stable in pH4.0 solution. The redox couple, A1/A2, with formal potential 0.58 V in pH1.0 and 0.44 V in pH4.0 solution, is due to the polymer and the corresponding current peak increase in height with each cycle, reflecting polymer growth.

Peak C is most probably due to monomer reduction, which in pH4.0 solution appears as two peaks (C1 and C2) due to same intermediate forms mentioned above. With the increase in the number of scans, these two peaks decrease in size and the peak potential values begin to overlap and become one peak, similar to what is found in pH1.0 solution. At lower pH values, as observed in sulphuric acid and also in McIlvaine's buffer pH2.0 (not shown), the polymer A1/A2 current peaks are already high in the second scan and then increase very little. This can be due to strong monomer adsorption, which also hinders polymer growth. At pH3.0 and 4.0, the increase is more gradual, leading to a more homogenous and compact polymer film. At pH5.0 and 6.0, a very small or no increase of current peaks was observed. Thus, PBG film formation is feasible over a wide range of pH, but film growth in pH3.0 and 4.0 electrolytes occurs in a more regular fashion. In pH4.0 solution, the increases of the polymer current peaks A1/A2 were two- and fivefold higher for oxidation and reduction, respectively, compared to pH3.0. Thus, polymer films were prepared from this electrolyte in all further experiments.

Three different monomer concentrations were investigated: 0.1, 0.5 and 1.0 mM (not shown). Increasing the monomer concentration led to an increase in the polymer current peaks A1/A2 by a factor of two. Since the largest currents were obtained for 1.0 mM brilliant green, this concentration was chosen for further polymerisation studies.

The mechanism of polymerisation is based on the following: if the parent molecule contains primary or secondary amino groups, the cation radical is formed at a lower potential than that of oxygen evolution and this radical then attacks the benzene ring in a free ortho position of the amino group [28]. A proposed form of a trimer is shown in Scheme 1b.

Polymerisation on top of CNT was performed using the experimental conditions optimised for CFEs without CNT: CV in 1 mM BG/McIlvaine's buffer pH4.0. The same cycling parameters were used, scanning between −1.0 and 1.2 V at 100 mV s^{-1}, but the number of cycles was increased to 20 because it was observed that film growth was continuing, whilst for electrodes unmodified by CNT, the currents reached a maximum after six to seven scans. Polymerisation at CNT/CFE is shown in Fig. 1c. The oxidation and reduction peak currents corresponding to polymer (A1 and A2) increase with each scan, faster in the first seven to eight cycles and then slowly until the 20th scan. This led to a more compact film. The value of the polymer peak currents is around 400 times higher both for oxidation and reduction, compared with PBG/CFE. The PBG peak potentials at CNT/CFE are almost 100 mV less positive, both for oxidation and reduction,



Scheme 1 **a** Chemical structure of brilliant green (BG) and **b** proposed structure for a BG trimer

than at unmodified CFE; however, the process is less reversible, since the peak potential difference (ΔE) is higher than at unmodified electrodes. A change in the peak potential values of the polymer deposited on CNTs compared with bare CFE was also observed in Ref. [29] for poly(neutral red) and poly(brilliant cresyl blue) and is probably due to the nanotube structure. All these results led to the conclusion that polymerisation of brilliant green at CNT carbon film-modified electrode is significantly better than on bare CFEs.

Characterisation of the modified electrodes

The properties of the PBG films on carbon film (PBG/CFE) and on carbon film modified with CNTs (PBG/CNT/CFE) were evaluated using CV, EIS and SEM.

Cyclic voltammetry

PBG-modified electrodes obtained by potential cycling and potentiostatically were characterised by CV in electrolytes with different pH values ranging from 1.0 to 7.0. For both electrode modification methods and in all electrolytes, one redox peak appears, corresponding to polymer oxidation/reduction, A1/A2. Figure 2a shows voltammograms for PBG/CFE formed by CV. It was observed that this process was pH-dependent, with the polymer peak potentials moving to less positive values with increase in pH; the slope of the midpoint potential (E_m) vs. pH is 51 mV per pH unit over the range studied (Fig. 2b). This value indicates that an equal number of protons and electrons are involved in the electrochemical process, as observed for other phenazine polymers [2, 4]. The anodic peak current values vary less than the cathodic ones; however, they are largest in acidic media, in neutral media being around 76 % of the maximum observed in pH3.0 solution (Fig. 2b). A similar tendency was observed for poly(brilliant cresyl blue) with maximum at pH4.0 [4]. The stability of the polymer film was examined by performing 30 consecutive cycles in McIlvaine's buffer pH7.0. A small 7 % decrease in the oxidation peak current was observed; however, the reduction peak decreased by 23 %. PBG deposited potentiostatically exhibited a similar pH-dependent behaviour, the slope of E_p vs. pH being 59 mV per pH unit.

The quantity of polymer deposited by each technique was calculated using Faraday's law, assuming that two electrons are involved in the redox reaction, similar to poly(MG) [3]. The charge was calculated by integration under the oxidation peak of the cyclic voltammogram in McIlvaine's pH4.0. The values found were 2.1 and 65 $\mu C\,cm^{-2}$ for PBG deposited by CV and potentiostatically, respectively. The surface coverage according to expression $\Gamma = Q/nFA$ (n is the number of electrons, F the Faraday constant and A the electrode area) was then determined as 1.1 $nmol\,cm^{-2}$ for the cyclic voltammetrically and 33.6 $nmol\,cm^{-2}$ for the potentiostatically prepared film. Thus, by the potentiostatic method, much more polymer is deposited; however, the film was less stable and leached from the electrode after only a little use. Taking into account these results, the decision was made to continue the study with the polymer film prepared by CV.

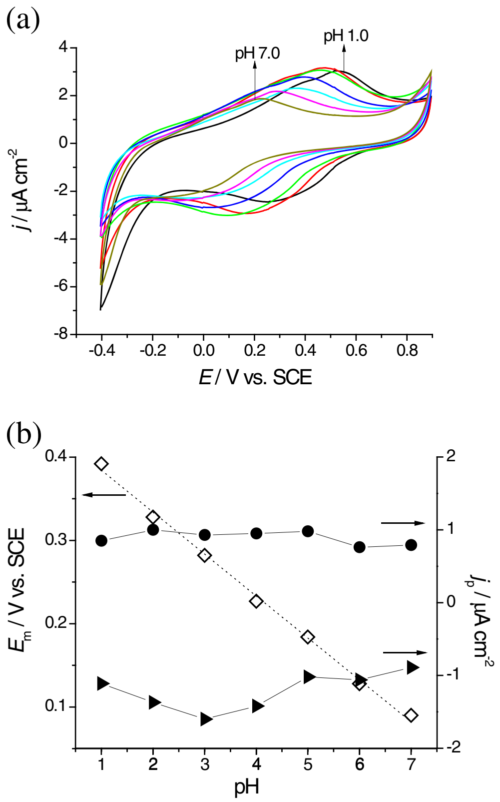


Fig. 2 **a** Cyclic voltammetry of PBG/CFE in different buffer pH. **b** Dependence on buffer pH of midpoint potential and anodic and cathodic current peaks of PBG-modified electrode

The PBG/CNT/CFE was also investigated in different pH electrolytes. In order not to destroy the CNT layer (which is soluble in acidic media), the study was performed only between pH4.0 and 7.0. The deposition of the PBG film above CNT led to no differences in the pH behaviour compared with PBG formed on CFE. In the pH range studied, it was seen that peak currents almost do not vary with pH and the midpoint peak potential dependence on pH is 51 mV/pH unit (not shown). The quantity of polymer deposited on CNT was determined as equivalent to 127.5 $nmol\,cm^{-2}$.

Electrochemical impedance spectroscopy

Modified and unmodified electrodes were studied by EIS in 0.1 M phosphate buffer pH7.0 at 0.0 V vs. SCE, where the modified electrodes will be used for ascorbate sensors (see below); complex plane spectra are shown in Fig. 3. The

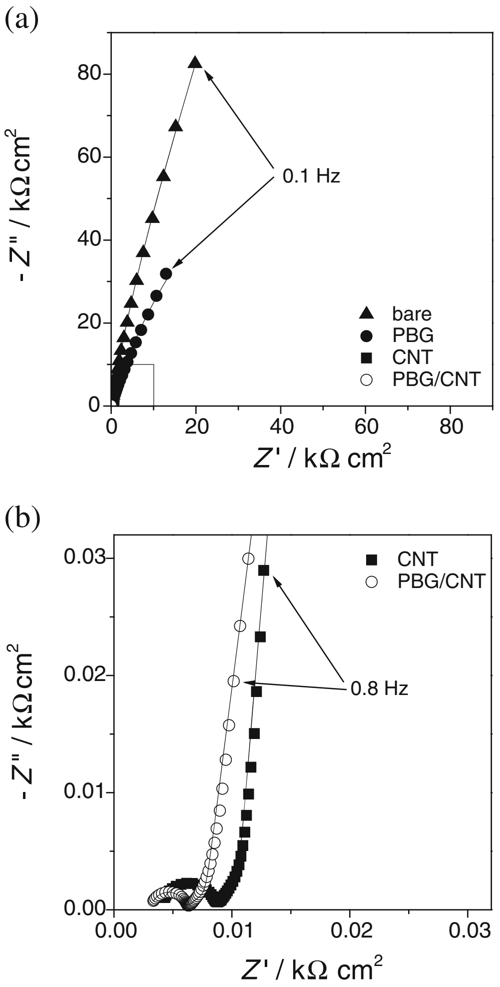


Fig. 3 **a** Complex plane impedance spectra for different electrodes: *filled triangle* bare, *filled circle* PBG, *filled square* CNT, *unfilled circle* PBG/CNT at 0.0 V in 0.1 M NaPBS, pH7.0. **b** Magnification of high frequency portion for CNT and PBG/CNT spectra

impedance values were the highest for the unmodified electrode, as expected and then decreased in the sequence PBG>CNT>PBG/CNT. At bare and PBG-modified electrodes, the spectra were modelled with a circuit comprising cell resistance, R_Ω, coupled with two parallel combinations, one containing a double layer capacitance, C_{dl}, and a charge transfer resistance, R_{ct}, and the other a constant phase element (CPE_2) with another resistance, R_2 (Fig. 4a). The CPE is modelled as a non-ideal capacitor ($CPE=-1/[i\omega C]^\alpha$), where ω is the angular frequency in radian per second and the exponent α reflects a non-uniform surface (α=1 corresponds to a perfectly uniform and smooth surface and α=0.5 to porous surface). For PBG-modified electrodes, the CPE is due to polymer film porosity (C_f) and the resistance is the film resistance, R_f.

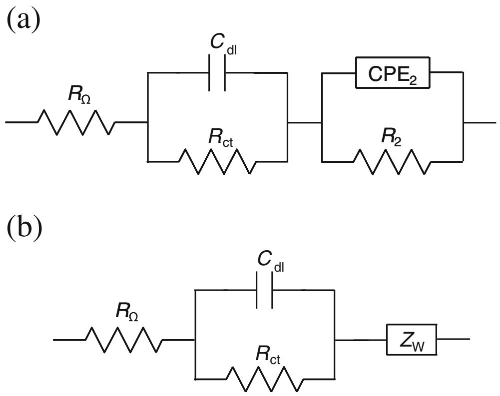


Fig. 4 Equivalent circuits used to fit the impedance spectra for: **a** CFE and PBG/CFE and **b** CNT/CFE and PBG/CNT/CFE

For CNT-modified electrodes and CNT with PBG, PBG/CNT, the spectra show a semicircular part at high frequency, corresponding to electron transfer, and a linear part at lower frequencies, corresponding to diffusion control. For these modifications, the circuit used (Fig. 4b) consists of the cell resistance, R_Ω; a capacitor, C_{dl}; a charge transfer resistance, R_{ct}; and an open Warburg element, W_0, representing diffusion through the film. The definition of the Warburg element used was:

$$Z_w(W_0) = R_{dif}\operatorname{ctnh}([i\tau\omega]^\alpha)/(i\tau\omega)^\alpha \qquad (1)$$

where R_{dif} is a diffusion resistance, τ is a time constant depending on the diffusion rate ($\tau=l^2/D$, where l is the effective diffusion thickness and D is the effective diffusion coefficient) and α=0.5 for a perfectly uniform flat interface.

The values obtained from equivalent circuit fitting are summarised in Table 1. The cell resistance was around 6Ω cm² for bare electrodes and 4Ωcm² for modified electrodes. From these data, it is seen that for PBG-modified electrodes, the double layer capacitance increases compared with unmodified electrodes, showing that the polymer film leads to greater charge separation at the interface and R_{ct} decreases. The small reduction in the value of the α exponent of the CPE in the PBG film to 0.75 suggests some porosity.

For CNT- and PBG/CNT-modified electrodes, R_{ct} is very low, so that this change can be ascribed to the presence of CNT, and C_{dl} is also much lower. The diffusion resistance decreases when PBG is placed on top of CNT, whereas the diffusion time, τ, increases, indicating that diffusion is slower due to a thicker film structure. The exponent α calculated from the open Warburg element were 0.47 for CNT and 0.46 for PBG/CNT electrodes, showing close to ideal infinite diffusion, which is usually found in thick films [30].

Scanning electron microscopy

SEM images can provide valuable information on electrode surface morphology. PBG, CNT and PBG/CNT films were prepared on ITO substrates under the same conditions as

Table 1 Data obtained from analysis of the impedance spectra for the modified electrodes in 0.1 M NaPBS at pH 7.0 using equivalent circuit fitting

Electrode	C_{dl} (μF cm^{-2})	R_{ct} (kΩcm^2)	C_2 (μF cm^{-2} s$^{\alpha-1}$)	α_2	R_2 (kΩcm^2)	R_{dif} (W_o) (Ωcm^2)	τ (W_o) (s)	α_2 (W_o)
CFE	18.8	588	56.2	0.81	10.9	–	–	–
PBG/CFE	36.4	183	60.5	0.75	12.5	–	–	–
CNT/CFE	6.27	0.0042				6.5	0.039	0.47
PBG/CNT/CFE	3.92	0.0028				5.0	0.054	0.46

those used to prepare the same films on CFE (CVs of modified ITO electrodes were similar to those on CFE). As shown in Fig. 5a, the PBG film forms aggregates on the electrode surface. The same behaviour was observed for poly(neutral red) [31] and poly(MG) [10]. In Fig. 5b, a micrograph of CNT shows the small bundle structure [32]. Figure 5c displays an image of the PBG/CNT film deposited that totally covers the electrode surface. Here, the MWCNT are not as visible, since they are covered by PBG. High aspect ratio structures are formed, showing an obvious increase of the amount of PBG deposited over the CNT and a non-compact structure in agreement with the increased amount calculated in "Cyclic voltammetry".

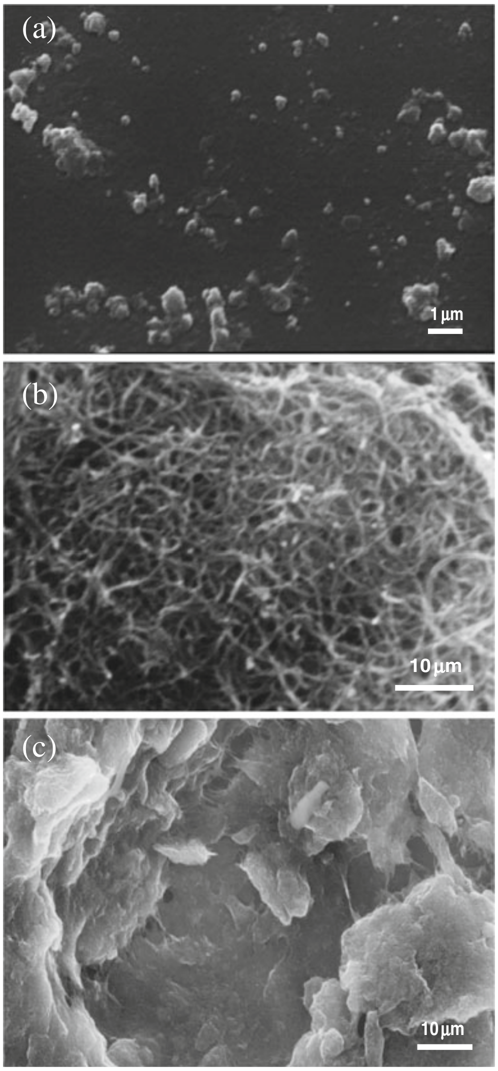


Fig. 5 SEM images of **a** PBG, **b** CNT and **c** PBG/CNT films on ITO electrodes

Electrochemical determination of ascorbic acid

The modified electrodes, PBG/CFE and PBG/CNT/CFE, were applied to the determination of AA by fixed potential amperometry. Although the pH characterisation of PBG-modified electrode showed that the best response was exhibited in acidic media, namely pH 3.0, the response at pH 7.0 is still good so the electrode could be used for determinations in natural samples at physiological pH. Hence, all measurements were carried out in 0.1 M sodium phosphate buffer, pH 7.0. Amperometry was carried out at 0.0 V vs. SCE, which is excellent for reducing interferences, such as uric acid or DA, which are known to oxidise at potentials that can be close to that of AA [33]. A well-defined response was obtained for both PBG and PBG/CNT sensors. Calibration curves showed linear ranges up to 100 and 200 μM, for PBG/CFE and PBG/CNT/CFE, respectively, with low detection limits of 5.1 and 2.4 μM. The sensitivity was very low at PBG/CFE (51.4 pA cm^{-2} μM^{-1}), most probably due to low polymer loading at the CFE, film instability and its quick deterioration by AA, besides being only at the beginning of the voltammetric wave. The sensitivity increased to 161 nA cm^{-2} μM^{-1} at PBG/CNT-modified electrodes.

The reproducibility and the relative standard deviation calculated from the sensitivity of three different electrodes prepared in the same way was 5.2 % for PBG and 2.1 % for PBG/CNT modified electrodes. The performance obtained using the PBG/CNT-modified electrode was compared with polymer-modified and modified carbon electrodes in the literature (see Table 2). Glassy carbon electrodes modified with poly(3,4-ethylenedioxythiophene) (PEDOT) exhibited good sensitivity (56.6 nA cm^{-2} μM^{-1}) but detected ascorbate only at higher concentrations, 500–3,500 μM at −2 mV vs. Ag/AgCl, with a higher detection limit of 7.4 μM [33]. The sensitivity is higher than in Ref. [34] in which a gold electrode was modified by fullerene C_{60} (3.3 μM) (49 nA cm^{-2} μM^{-1} with linear range between 0.1 and 1.0 mM) or in Ref. [35] with MWCNT covalently modified osmium-based

Table 2 Comparison of analytical parameters for ascorbate sensors at different modified electrodes. See text for explanation of symbols

Electrode	Potential (V vs. Reference)	Linear range (mM)	Sensitivity (nA cm^{-2}µM^{-1})	Detection limit (µM)	Reference
PEDOT/GCE	−0.002 (Ag/AgCl)	0.5–3.5	56.6	7.4	[33]
Fullerene C_{60}/Au	0.08 (Ag/AgCl)	0.1–1.0	49	3.3	[34]
MWCNT/CO-POs-EA/GCE	0.4 (Ag/AgCl)	0.0–0.1	42	[a]	[35]
NiNPs@P-1,5-DAN/GCE	0.1 (Ag/AgCl)	0.1–0.5	71	[a]	[36]
SWCNT-IL	0.005 (Ag/AgCl)	0.003–4.2	805	1.0	[37]
Q-Chit/C/PCE	0.1 (Ag/AgCl)	0.01–5.0	76	3.0	[38]
Poly(caffeic acid)/GCE	0.018 (Ag/AgCl)	0.02–1.2	152	9.0	[39]
PBG/CFE	0.0 V (SCE)	0.005–0.1	0.0514	5.1	This work
PBG/CNT/CFE	0.0 V (SCE)	0.005–0.2	161	2.4	This work

[a] Not specified

redox polymer or as in Ref. [36] at poly(1,5-diaminonaphtalene) (NiNPs@P-1,5-DAN). Although higher sensitivity, lower detection limit (1.0 µM) and wider linear range was obtained at ionic liquid single-wall CNT [37], sensor construction is more complex. At hydroquinone Chit carbon composite on plasma-treated printed carbon electrodes (Q-Chit/C/PCE) at 0.1 V vs. Ag/AgCl [38], the linear range is much longer (up to 5.0 mM) but the sensitivity is a factor of 3 lower than here and the detection limit is higher (3 µM). Lower sensitivity and higher detection limit (7 µM) than the present sensor were also exhibited by a poly(caffeic acid)-modified glassy carbon electrode [39].

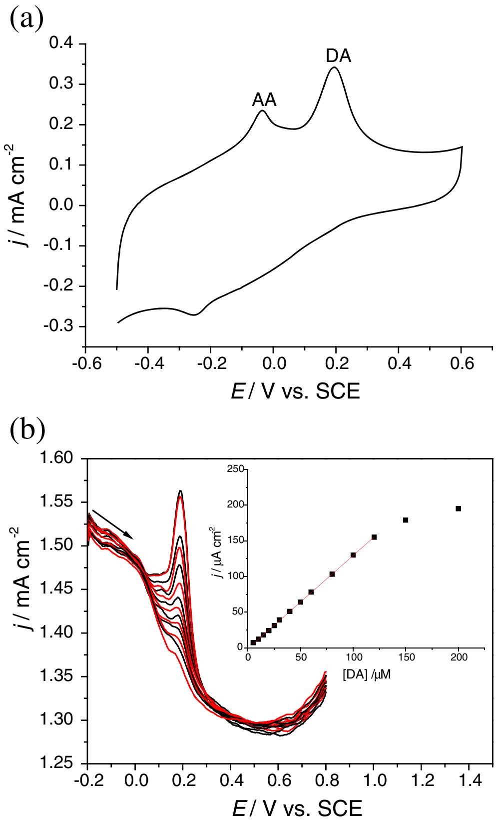


Fig. 6 **a** Cyclic voltammetry at a scan rate 10 mV s^{-1} in 0.1 M NaPBS pH7.0 with 600 µM AA and 40 µM DA. **b** Differential pulse voltammetry at PBG/CNT-modified CFE for the determination of dopamine in 0.1 M NaPBS pH7.0. *Inset* shows calibration curve

As an indicator of stability of the modified electrodes towards AA, their performance over a period of 16 days was measured, constructing calibration curves (eight injections) each day. After this period, the response of the PBG-modified electrodes dropped to 16 % of the initial value, whereas the PBG/CNT electrodes decreased by only 4 %.

Interferences and dopamine measurement

Although PBG/CNT-modified electrodes showed better response as well as stability, an examination of interferences was carried out at both type of electrodes, with and without nanotubes, in order to check selectivity and applicability. Interference studies were conducted by placing the modified electrodes in buffer, under continuous stirring and waiting for the baseline current to stabilise. After that ascorbate was injected, followed by the interferents and finally, the same

Table 3 Determination of ascorbate in pharmaceutical samples

Electrode	Added (mg)	Found (mg)	Recovery (%)
PBG/CFE	250 (paracetamol)	563±8.1 (paracetamol)	225
	240 (aspirin)	499±6.7 (aspirin)	207
PBG/CNT/CFE	250 (paracetamol)	265±5.2 (paracetamol)	106
	240 (aspirin)	248±4.1 (aspirin)	103

amount of ascorbate was injected again. Aspirin, acetaminophen (paracetamol), DA, salicylic acid and uric acid were tested, with their concentration chosen to be twice that of AA.

At PBG/CFE without CNT, interferences were observed: paracetamol increased the response of AA by 42 % and DA by 7 %, whilst salicylic acid decreased the response by 8 %. AA in the presence of all compounds presented a decrease of 68 % compared with that without interferents.

However, at PBG/CNT/CFE, the interferences were small: only DA exhibited a current response, corresponding to 8 % of that of the AA response and a small decrease of 4 % in the AA response was observed after injection of interfering compounds. Thus, at PBG/CNT sensors, the selectivity was greatly improved with respect to PBG alone and this electrode should be suitable for the determination of AA by standard addition.

CV was performed in order to investigate the behaviour of DA in the presence of AA (Fig. 6a). The peaks for the two compounds (E_{AA}=−0.035 V and E_{DA}=0.195 V) have a difference of 0.230 V, which is enough for determination of AA and DA without interference from each other. DPV, with step potential of 2 mV, pulse amplitude of 25 mV and scan rate of 10 $\mathrm{mV\,s^{-1}}$, was used to determine DA at the PBG/CNT electrode. Under these conditions, the DA response was linear between 5.0 and 120 μM (Fig. 6b), with a detection limit of 1.6 μM and sensitivity of 1.2 $\mu\mathrm{A\,cm^{-2}}\,\mu\mathrm{M}$. These results are promising for the determination of DA, even though the sensitivity is not as high as in Ref. [34] with fullerene C_{60}-gold electrode by square wave voltammetry (21.4 $\mu\mathrm{A}\,\mu\mathrm{M\,cm^{-2}}$) or in Ref. [40] with a glassy carbon electrode modified with MWCNT and Chit, which uses DPV (7.75 $\mu\mathrm{A\,cm^{-2}}\,\mu\mathrm{M}$) after 50-s pre-concentration. However, the sensitivity can be improved by optimising the parameters for DPV determination and also including pre-concentration.

Measurements in pharmaceutical samples

Amperometric determination of AA in pharmaceutical samples was carried out using the PBG/CNT- and PBG-modified electrodes. Two commercial tablets of aspirin and paracetamol, both containing vitamin C, were dissolved as described in the experimental section. The samples were analysed in triplicate by the standard addition method: the sample was first added, followed by four additions of standard ascorbate solution, determining the concentration of sample from the linear regression parameters. The values obtained are presented in Table 3. At PBG/CNT electrodes, the content of AA found in tablets was 265±5.2 mg for paracetamol and 248±4.1 mg for aspirin and recoveries were 106 % and 103 %; the results were not acceptable at PBG-modified electrodes owing to interferences. Thus, PBG by itself is not suitable for determination in this type of natural sample, but with CNT, the improvement in selectivity leads to good and acceptable sensor precision for ascorbate determination.

Conclusions

PBG has been formed, for the first time, on top of CFEs without and with deposited CNTs. The modified electrodes were characterised by CV, EIS and SEM. It was observed that by itself, PBG forms aggregates and is not very stable; however, when polymerised on top of CNT, the resulting composite completely covers the electrode surface and the assembly is much more stable. Modified electrodes were applied to the determination of ascorbate by fixed potential amperometry with PBG/CNT-based sensors giving a performance comparable or better than in the literature, with a simple construction procedure. Recovery measurements in pharmaceutical samples showed that they can be successfully employed for this purpose. The large peak separation between AA and DA facilitates the determination of DA and AA simultaneously by DPV.

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