Methylene Blue/Multiwall Carbon Nanotube Modified Electrode for the Amperometric Determination of Hydrogen Peroxide

Roselyn C. Peña,[a] *Mauro Bertotti*,[a] *Christopher M. A. Brett**[b]

[a] Instituto de Química, Universidade de São Paulo, 05508-900 São Paulo, Brasil
[b] Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3004-535 Coimbra, Portugal
Tel/fax: +351–239835295
*e-mail: brett@ci.uc.pt

Received: June 19, 2011
Accepted: July 22, 2011

Abstract
A novel amperometric sensor based on the incorporation of multiwalled carbon nanotubes (MWCNT) into a poly(methylene blue) (PMB) film immobilized on carbon composite electrodes is described. Cyclic voltammetry indicated that at a surface covered by a MWCNT/PMB layer the cathodic reduction of hydrogen peroxide is facilitated and occurs already at 0.0 V versus SCE. The effect of the order of deposition of PMB and MWCNT, as well as its loading, on electrochemical behaviour was evaluated by cyclic voltammetry and electrochemical impedance spectroscopy. The influence of the various immobilised platforms on the electrocatalytic performance towards hydrogen peroxide was also examined.

Keywords: Multiwalled carbon nanotubes, Poly(methylene blue), Hydrogen peroxide, Modified electrode

DOI: 10.1002/elan.201100324

1 Introduction

CNTs have special properties depending on their dimensionality, structure and topology. The basic constitution of the nanotube lattice is the C–C covalent bond, as in layers of graphite. Therefore, carbon nanotubes can be found with nominal sp^2 hybridisation [1]. Carbon nanotubes have been described as being able to exist as a single-walled nanotube (SWCNT) or as a multiwalled nanotube (MWCNT), which consists of several concentric cylinders of graphite, 0.34 to 0.36 nm spaced from one another. This spacing is slightly higher than the interplanar distance of graphite [2].

Carbon nanotubes (CNTs) are interesting materials due to their electrical, structural and mechanical properties and make them highly promising nanoscale building blocks for the construction of novel functional materials and potential candidates for the fabrication of sensors and biosensors [3–6].

CNTs behave electrically as a metal or like a semiconductor and have the ability to promote electron transfer reactions [7]. The electronic properties of these materials have been explored as a means of promoting electron transfer reactions for a wide range of species of biological relevance, including DNA [8], proteins [9], hydrogen peroxide [10], dopamine [11] and ascorbic acid [12].

The manufacture of CNTs/conducting polymer composites has generated great interest since CNTs can improve the electrical and mechanical properties of polymers [13]. The structure of conjugated π bonds of CNTs allows them to interact with the aromatic polymer through π–π bonds. The immobilisation of CNTs/polymer composites on electrode surfaces has generated a wide variety of new platforms with excellent features which are attractive for many practical applications. The electropolymerisation of thin films has been shown to be a powerful tool in the development of electrochemical sensors. The technique allows the construction of films based on monomers, hence ultrafine structures with electrochemical properties indicated for use in the fabrication of electrochemical sensors and biosensors can be obtained [14–16].

Poly(methylene blue) (PMB), shown in Scheme 1a, has been widely used as electrocatalyst for the oxidation of haemoglobin [17] and NADH [18], since this compound has good electrocatalytic properties. Studies on the influence of pH on the electropolymerisation of MB [19] reported that better results were obtained in alkaline conditions (pH 9.2). The effect of the counter ion was also examined and it was concluded that a more efficient film growth occurred in solutions containing sulphate, suggesting that the presence of this anion has an electrocatalytic effect on the electropolymerisation process.

Hydrogen peroxide is an essential compound in the textile, pulp and paper industry and in some areas of food and medicine [20,21]. Hydrogen peroxide is also used to remove pollutants from waste water as it can safely be used as part of a cost-effective approach which utilizes the Fenton's reaction [22]. Electrochemical sensors for the determination of hydrogen peroxide have advantages based on low detection limits, good selectivity, fast response time, miniaturisation and portability [23]. However, these characteristics depend on the use of mediators capable of recognizing the analyte in complex samples and different materials have been used to reduce the overpotential required for the reduction of hydrogen peroxide [14,24–32]

The association between the PMB film and carbon nanotubes may represent a new sensing platform for the electrochemical determination of hydrogen peroxide. In the present paper, we report the modification of a carbon composite (CC) modified electrode containing CNTs and comparing this sensor to another also containing electropolymerized MB with respect to the electrocatalysis of hydrogen peroxide reduction.

2 Experimental

2.1 Reagents and Solutions

Multiwalled carbon nanotubes (MWCNT) were obtained from NanoLab, USA, with ~95 % purity, 30 ± 10 nm diameter and 1–5 µm length. MWCNT functionalisation was performed with *N*,*N*-dimethylformamide (DMF) (Fluka, Switzerland) and nitric acid (Riedel-de Haën, Germany). Methylene blue monomer (MB) was acquired from Aldrich (Germany). The buffer solution used for electropolymerisation of MB was a 0.025 mol L^{-1} sodium tetraborate saline solution which was prepared from disodium tetraborate 10-hydrate (Merck, Germany), sodium hydroxide (Riedel-de-Haën, Germany) with addition of 0.1 mol L^{-1} Na_2SO_4 (Merck, Germany). MB concentration in the buffer solutions was 1 mmol L^{-1}.

The electrolytes used for the characterisation of the phenothiazine-modified electrodes were 0.1 mol L^{-1} KCl (Fluka, Switzerland) and 0.01 mol L^{-1} HCl (37 % Riedel-deHaën, Germany). 35 % (m/v) hydrogen peroxide (José M. Vaz Pereira, Portugal) solutions were freshly prepared for each experiment and standardized by permanganate titration. All other reagents employed were analytical grade. Distilled, deionised water was used throughout (Millipore Milli-Q nanopure water).

2.2 Instrumentation

Measurements were performed in a 15 mL, one-compartment cell containing the carbon composite (CC) modified electrode (geometric area 0.07 cm^2) as working electrode, a platinum foil auxiliary electrode and a saturated calomel electrode (SCE) as reference. Voltammetric and amperometric experiments were carried out using a PalmSens potentiostat (Pamsens BV, Houten, Netherlands). Electrochemical impedance measurements were carried out with a PC-controlled Solartron 1250 Frequency Response Analyser coupled to a Solartron 1286 electrochemical interface (Solartron Analytical, UK) using ZPlot 4.1 software (Scribner Associates, USA). A sinusoidal voltage perturbation of amplitude 10 mV rms was applied in the frequency range between 65 kHz and 0.1 Hz with 10 frequency steps per decade. The spectra were recorded at a potential of 0.0 V versus SCE. Fitting was done using ZView 3.2 software (Scribner Associates, USA). The pH measurements were performed with a CRISON 2001 micro pH-meter. Experiments were carried out at room temperature, 25 ± 1 °C.

2.3 Preparation of Polymer-Modified Electrodes

The working electrode was pre-treated by applying a fixed potential of +0.9 V vs. SCE during 240 s and then by cycling the potential between −1.0 and 1.0 V versus SCE at a scan rate of 100 mV s^{-1}, until a reproducible voltammogram was obtained. The supporting electrolyte solution was used in the pretreatment step and the electropolymerisation procedure was carried out in the same solution also containing 1 mmol L^{-1} MB. The polymer was synthesized under potentiodynamic conditions by scanning the potential between −0.75 and 1.0 V versus SCE at a scan rate of 50 mV s^{-1}.

2.4 MWCNT Functionalisation

A mass of 100 mg of MWCNT was stirred in 10 mL of a 3 mol L^{-1} nitric acid solution for 24 h. The solid product was collected on a filter paper and washed several times with nanopure water until the pH of the remaining solution became close to 7. The functionalised MWCNTs obtained were then dried in an oven at 80 °C for 24 h.

The dried MWCNTs were dispersed in DMF 1 % (v/v), and sonicated for 4 h to ensure a homogeneous mixture. The MWCNT coating was prepared by dropping 2.5 µL of the MWCNT/DMF dispersion on the surface of the CC electrode using a micropipette and allowing it to dry at room temperature.

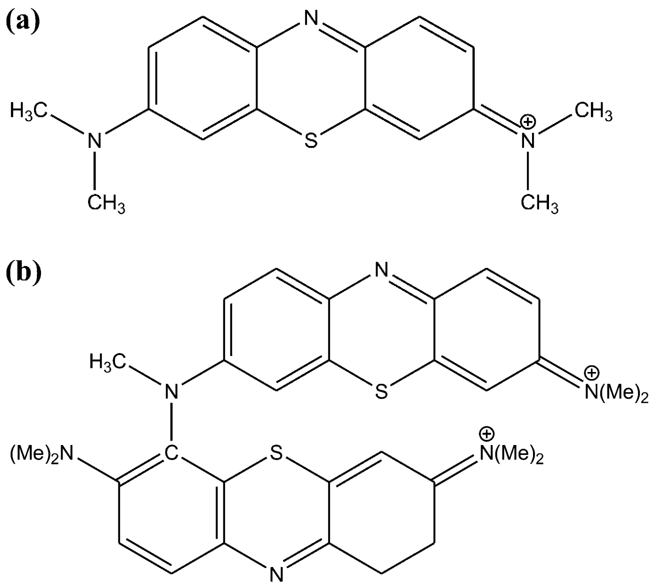
Different procedures were employed to modify the CC electrodes in order to examine the best response of the fabricated sensors towards hydrogen peroxide:

- The film of methylene blue was electrodeposited on the CC electrode surface without the incorporation of MWCNTs (PMB/CC).
- The CC electrode was modified with a dispersion of 25 (MWCNTs25/CC) or 50 (MWCNTs50/CC) µg of MWCNTs.
- The CC electrode was modified with a dispersion of 25 or 50 µg of MWCNTs, followed by electropolymerisation of methylene blue (PMB/MWCNTs25/CC and PMB/MWCNTs50/CC).
- The electropolymerisation of methylene blue was carried out prior to coating with a dispersion of 25 or 50 µg of MWCNTs (MWCNTs25/PMB/CC and MWCNTs50/PMB/CC).

3 Results and Discussion

3.1 Electrochemical Characterisation

The pH of the buffer solution has a significant influence on the formation of the PMB film, as previously reported [19]. The irreversible oxidation of the monomer and the formation of a cation radical, which is unstable and binds with other radicals through the amino group [33], is a key step in the polymerisation process. It is likely that before formation of the radical cation species, one of the substituents of the amino group is oxidised in a mechanism involving hydroperoxide. These anions can attack one of the methyl groups of the tertiary amino group bound to the aromatic ring [19]. The formation of the dimer is represented in Scheme 1b.



Scheme 1. Chemical structures of the methylene blue monomer (a) and of its dimer (b).

Figure 1 shows the typical growth of a PMB film in an experiment carried out in a supporting electrolyte solution containing the monomer by using two different working electrodes: a MWCNTs50/CC electrode (Figure 1a) and a CC electrode (Figure 1b). Electropolymerisation of the monomer starts at a potential near to −0.3 V vs. SCE, and a peak corresponding to polymer formation is clearly noticed at −0.058 V vs. SCE in the 30th cycle (Figure 1a). By comparing both figures one can see a current enhancement in the presence of MWCNTs due to the increased surface area provided by the carbon nanotubes [34].

Typical examples of cyclic voltammograms recorded using the different modifications in solutions containing hydrogen peroxide are shown in Figure 2. As seen from Figure 2A, the electroreduction of hydrogen peroxide at the MWCNTs50/CC modified electrode occurred irreversibly, starting at around +0.3 V vs. SCE, a potential similar to that with the MWCNTs50/PMB/CC modified electrode (Figure 2B). Therefore, MWCNTs have an electrocatalytic effect on the reduction of hydrogen peroxide. The electrocatalytic activity of the PMB/MWCNTs50/CC modified electrode towards the cathodic reduction of hydrogen peroxide is demonstrated in Figure 2C. A significant current enhancement is found upon addition of hydrogen peroxide, but this process occurs at more negative potentials in comparison to what is observed with the MWCNTs50/PMB/CC modified electrode (Figure 2B). By comparing these results, it seems that MWCNTs are distributed throughout the PMB film in the MWCNTs50/PMB/CC structure and are exposed directly to hydrogen peroxide, whereas the same interaction is unable to occur when the PMB film is coated after immobilisation of MWCNTs in the PMB/MWCNTs50/CC modified electrode. Hence, MWCNTs50/PMB/CC operating at 0.0 V was selected as the most favourable modified electrode combination for analytical applications, taking into account the selectivity of the measurements.

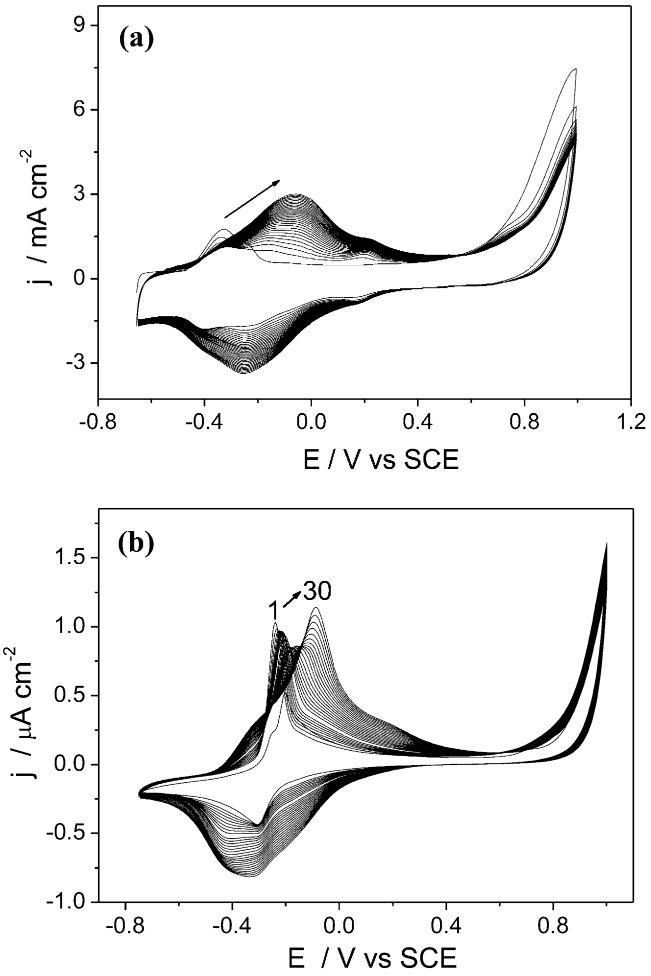


Fig. 1. Cyclic voltammograms recorded during the electropolymerisation of MB on a (a) MWCNTs50/CC electrode (b) CC electrode in a solution containing 1 mmol L^{-1} MB + 0.025 mol L^{-1} $Na_2B_4O_7$ + 0.1 mol L^{-1} Na_2SO_4; 30 cycles between −0.65 and +1.0 V vs. SCE at scan rate 50 mV s^{-1}.

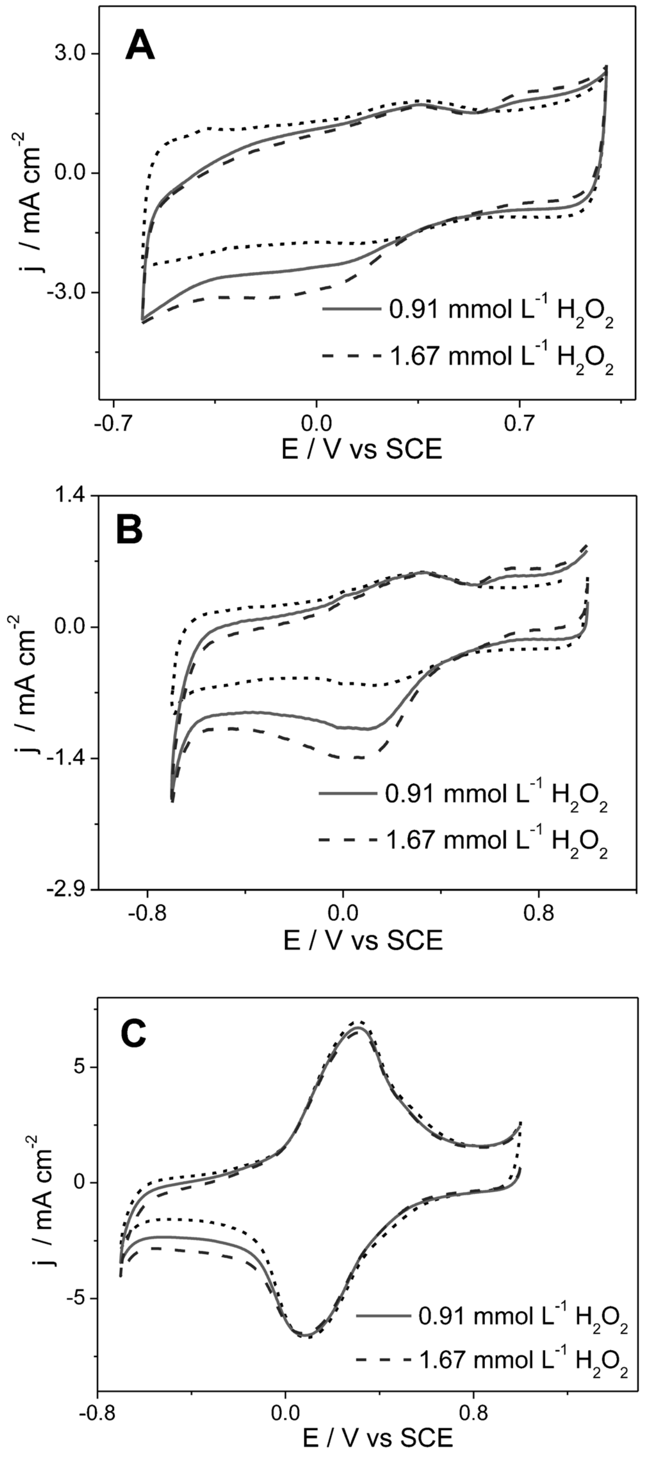


Fig. 2. Cyclic voltammograms recorded in a solution containing 0.1 mol L^{-1} KCl + 0.01 mol L^{-1} HCl solution before and after addition of hydrogen peroxide (final concentration 0.91 and 1.67 mmol L^{-1}) by using: (A) MWCNTs50/CC, (B) MWCNTs50/PMB/CC and (C) PMB/MWCNTs50/CC modified electrodes. Scan rate = 50 mV s^{-1}.

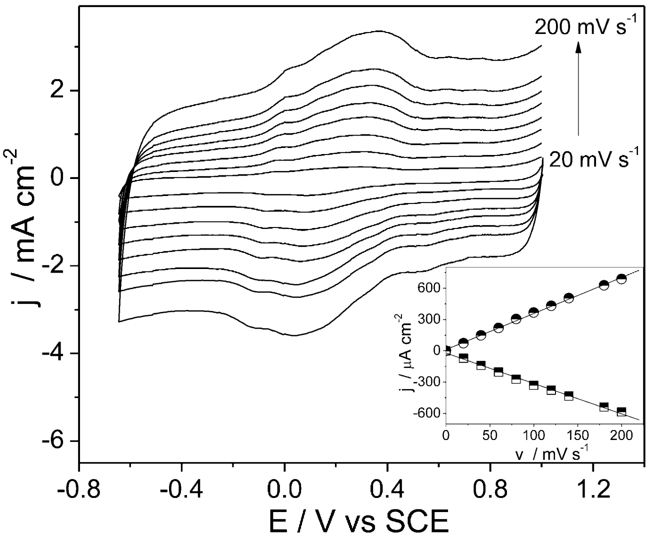


Fig. 3. Cyclic voltammograms recorded with the MWCNTs50/PMB/CC modified electrode in a 0.1 mol L^{-1} KCl + 0.01 mol L^{-1} HCl solution at different scan rates from 20 to 200 mV s^{-1}. Inset: Dependence of anodic and cathodic peak currents as a function of scan rate.

The scan rate dependence of the oxidation and reduction peak currents of immobilised MWCNTs50/PMB/CC up to 200 mV s^{-1} follows a characteristic linear law (Figure 3), which provides evidence of a surface-confined reaction.

Electrochemical impedance spectroscopy was used to examine the interfacial properties of different structures immobilised on the surface of the CC electrode. The measurements were carried out in a 0.1 mol L^{-1} KCl + 0.01 mol L^{-1} HCl solution. Figure 4a shows impedance spectra obtained at 0.0 V vs. SCE for various modified electrodes with MWCNT and PMB.

Modelling of the spectra was done using the equivalent circuit shown in Figure 4b. The equivalent circuit consists of a cell resistance R_Ω, in series with C_f and R_f in parallel, representing the capacitance and the resistance of the film, respectively. The reactions at the redox centres within the porous film layer is represented by a series mass transport finite diffusion Warburg element Z_w. This last element manifested itself at high frequency and was found to be necessary in order to obtain good fitting. The analysis to be presented will concentrate on C_f and R_f, representative of the bulk film characteristics at this potential. The cell resistance is $2.3 \pm 0.2\ \Omega\ cm^2$ in all spectra.

At unmodified CC electrodes, film resistance and capacitance values of 13.0 Ω cm^2 and 196 μF cm^{-2} were found, whereas these values for PMB/CC became 11.6 Ω cm^2 and 3.07 mF cm^{-2}. Hence, the PMB/CC modified electrode is slightly more conductive than the CC unmodified electrode polarised at 0.0 V and charge separation significantly greater, reflecting the existence of redox-active sites, in this potential region where oxidation and reduction of the polymer takes place.

Table 1 shows resistance and capacitance values obtained by fitting the impedance spectra for the various types of modified electrode with MWCNT. There is some error associated with the R_f values since only the initial

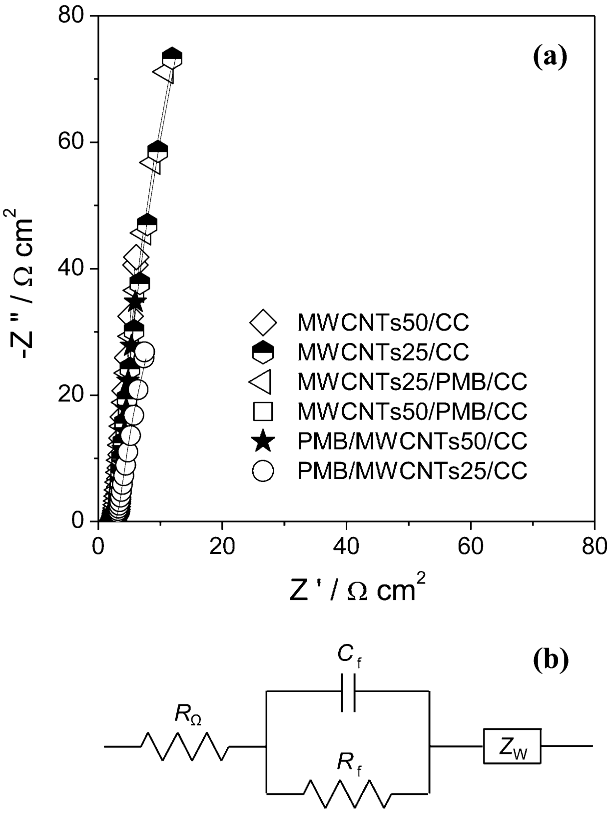


Fig. 4. (a) Complex plane impedance spectra for different modified electrodes obtained in a 0.1 mol L^{-1} KCl + 0.01 mol L^{-1} HCl solution, $E = 0.0$ V vs. SCE. (b) Equivalent circuit used for fitting of electrochemical impedance spectra; see text for the meaning of symbols.

part of the semicircle could be recorded; however, the error in the C_f values is low (<0.5 %) so that the discussion will concentrate on these values.

Capacitance values are much larger than without MWCNT and increase with loading, as does the film resistance (thicker film). Smaller capacitance and resistance values are observed for MWCNT25/CC and PMB/MWCNT25/CC modified electrodes. This may be attributable to the smaller amount of MWCNTs on the electrode surface and can be confirmed by comparing structures containing different amounts of CNTs. For instance, the C_f value increased from 64.7 mF cm^{-2} to 101.8 mF cm^{-2} on changing from MWCNTs25/PMB/CC to MWCNTs50/PMB/CC. In conclusion, one can observe that modification with higher amounts of MWCNTs leads to higher capacitance values, reflecting faster electron transfer kinetics at the modified electrode.

Table 1. Equivalent circuit fitting to impedance spectra for MWCNTs50/PMB/CC modified electrodes in 0.1 mol L^{-1} KCl + 0.01 mol L^{-1} HCl solution at 0.0 V. See text for meaning of symbols.

Structure	C_f (mF cm^{-2})	R_f (kΩ cm^2)
MWCNTs50/CC	39.5	1.34
MWCNTs25/CC	20.9	0.68
MWCNTs50/PMB /CC	101.8	2.11
MWCNTs25/PMB /CC	64.7	0.27
PMB/MWCNTs 50/CC	47.7	2.24
PMB/MWCNTs 25/CC	21.5	0.82

3.2 Analytical Applications

The influence of the modifier film on the response to hydrogen peroxide was examined by amperometry using seven different types of modified electrode. Taking into account the selectivity of the amperometric determinations, the potential selected was 0.0 V. At this potential, the MWCNTs50/PMB/CC structure showed the best sensitivity, as seen in the calibration plots in Figure 5. It should be noted that at more negative potentials the relative sensitivities changed.

Figure 6 shows the results of a typical amperometric experiment performed with the MWCNTs50/PMB/CC modified electrode operating potentiostatically at 0.0 V vs. SCE in a stirred solution. From the Inset of this figure it can be seen that the sensor gave a linear current response in the range 109 to 3000 μmol L^{-1} with a sensitivity of 108 μA $mmol^{-1}$ L cm^{-2}. The detection and quantification limits were calculated as 20.7 ($S/N = 3$) and 69.1 ($S/N = 10$) μmol L^{-1}.

The analytical performance of the MWCNTs50/PMB/CC modified electrode was compared with that of different sensors described in the literature, summarised in Table 2. It may be noted that the proposed modified electrode has an extended linear concentration range and a good detection limit. Even though the developed sensor is not as sensitive as a few of those reported in the literature, it has an important advantage in that it can be operated at 0.0 V. At such a relatively positive potential, elec-

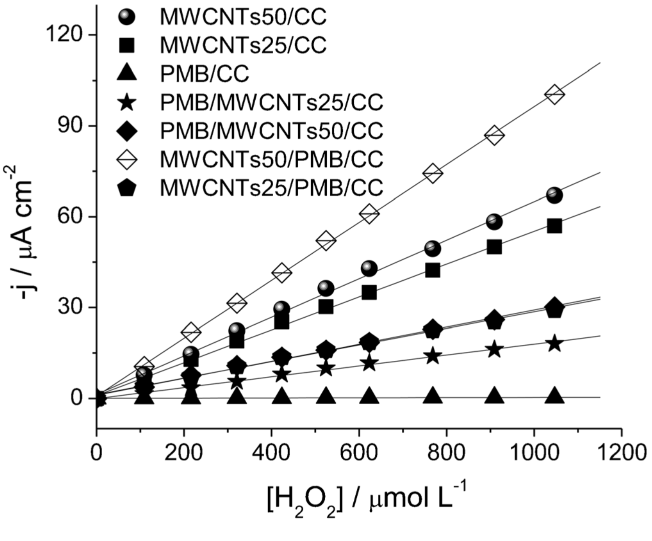


Fig. 5. Calibration plots for the different types of modified electrodes in 0.1 mol L^{-1} KCl + 0.01 mol L^{-1} HCl solution upon addition of hydrogen peroxide from 109 to 1047 μmol L^{-1}. $E = 0.0$ V vs. SCE.

Table 2. Comparison of the MWCNTs50/PMB/CC modified electrode with other H_2O_2 sensors.

Electrode	Detection potential (V)	Sensitivity (μA $mmol^{-1}$ L cm^{-2})	Linear range (μmol L^{-1})	Detection limit (μmol L^{-1})	Ref.
Nano-MnO_2	+0.65	266	0.12–2160	0.08	[35]
MnO_2/Nafion/GCE	+0.80	514	10–150	2.0	[36]
PBCB [a]	0.00	0.96	0–65	4.2	[33]
CuO nanowires	−0.2	30.1	10–2887	–	[37]
SnHCF [b]	−0.1	5.88×10^{-4}	4–50	1.	[38]
PNRNWs [c]	−0.1	318	1–8000	1.00	[39]
MWCNTs50/PMB/CC	0.0	108	100–3000	21.7	This work

[a] poly(brilliant cresyl blue); [b] Sn hexacyanoferrate; [c] poly(neutral red) nanowires.

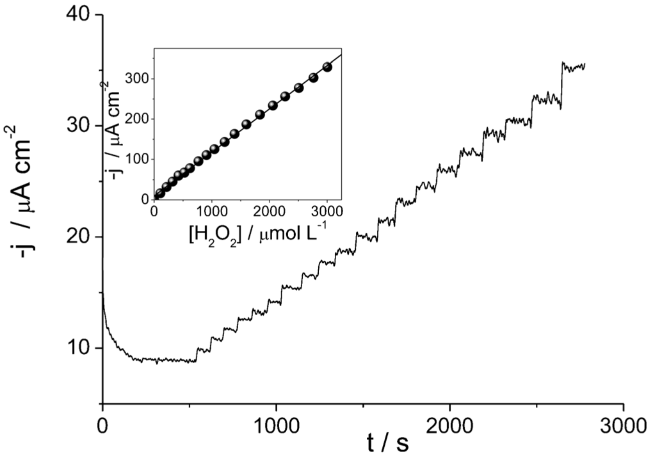


Fig. 6. Current responses monitored as a function of time with the MWCNTs50/PMB/CC modified electrode in 0.1 mol L^{-1} KCl + 0.01 mol L^{-1} HCl supporting electrolyte during repetitive additions of hydrogen peroxide; $E = 0.0$ V. Inset: Calibration plot.

tron transfer reactions involving other species are few, thus avoiding effects from interfering species.

The repeatability of the method was evaluated by calculating the relative standard deviation of repetitive cyclic voltammograms recorded in a 1.96 mmol L^{-1} H_2O_2 + 0.1 mol L^{-1} KCl + 0.01 mol L^{-1} HCl solution and the relative standard deviation was found to be 1.6%. The long-term stability of the MWCNTs50/PMB/CC modified electrode was also examined. It is an added advantage that the film of PMB anchors the MWCNT deposited afterwards, leading to a sensor which is more robust than that with MWCNT by itself. The results revealed that the current response remains constant after four hours, indicating that proposed sensor is suitable for analytical applications.

4 Conclusions

In this work we have demonstrated that the deposition of a layer of PMB onto electrode surfaces promotes a more efficient electroreduction of hydrogen peroxide. The incorporation of MWCNTs on a CC electrode onto which a film of PMB has been previously immobilized provides a sensor which has distinguishable features for hydrogen peroxide analysis, and this enhancement in sensitivity is attributable to the increase in surface area. The MWCNTs50/PMB/CC modified electrode has a linear response over a wide range of concentration, with low detection limit and good repeatability. Since the sensor operates at applied potentials around 0.0 V, interfering species are likely to be electroinactive. The attractive features of the proposed platform raise potential possibilities for its application as a practical sensor for hydrogen peroxide determinations.

Acknowledgements

R. Peña thanks *Banco Santander* for a study grant through the International Postgraduate Mobility Programme to the University of Coimbra. The authors thank *FAPESP* (*Fundação de Amparo à Pesquisa do Estado de São Paulo*), *CAPES* (*Coordenação de Aperfeiçoamento de Pessoal de Nível Superior*), *CNPq* (*Conselho Nacional de Desenvolvimento Científico e Tecnológico*) for financial support). Financial support from *Fundação para a Ciência e a Tecnologia* (*FCT*), PTDC/QUI/65732/2006 and PTDC/QUI-QUI/116091/2009, POCI 2010 and *COMPETE* (co-financed by the European Community Fund FEDER) and *CEMUC* (Research Unit 285), Portugal, is also gratefully acknowledged.

References

[1] D. Du, M. H. Wang, J. M. Zhang, H. Cai, H. Y. Tu, A. D. Zhang, *Electrochem. Commun.* **2008**, *10*, 85.
[2] P. M. Ajayan, *Chem. Rev.* **1999**, *99*, 1787.
[3] H. Kroto, H. Terrones, *Interdiscip. Sci. Rev.* **2000**, *25*, 78.
[4] S. Reich, C. Thomsen, J. Maultzsch, *Carbon Nanotubes: Basic Concepts and Physical Properties*, Wiley-VCH, Weinheim **2004**.
[5] J. J. Gooding, *Electrochim. Acta* **2005**, *50*, 3049.
[6] K. B. Male, S. Hrapovic, J. H. T. Luong, *Analyst* **2007**, *132*, 1254.
[7] C. N. R. Rao, *Abstr. Pap. Am. Chem. Soc.* **2001**, *221*, 645.
[8] K. B. Wu, J. J. Fei, W. Bai, S. S. Hu, *Anal. Bioanal. Chem.* **2003**, *376*, 205.

[9] G. C. Zhao, L. Zhang, X. W. Wei, Z. S. Yang, *Electrochem. Commun.* **2003**, *5*, 825.
[10] J. Wang, M. Musameh, *Anal. Chem.* **2003**, *75*, 2075.
[11] Y. Y. Sun, K. B. Wu, S. S. Hu, *Chem. J. Chin. Univ.-Chin.* **2002**, *23*, 2067.
[12] H. X. Luo, Z. J. Shi, N. Q. Li, Z. N. Gu, Q. K. Zhuang, *Anal. Chem.* **2001**, *73*, 915.
[13] P. Du, S. N. Liu, P. Wu, C. X. Cai, *Electrochim. Acta* **2007**, *53*, 1811.
[14] A. A. Karyakin, E. E. Karyakina, L. Gorton, *Electrochem. Commun.* **1999**, *1*, 78.
[15] A. A. Karyakin, O. A. Bobrova, E. E. Karyakina, *J. Electroanal. Chem.* **1995**, *399*, 179.
[16] R. Pauliukaite, M. E. Ghica, M. M. Barsan, C. M. A. Brett, *Anal. Lett.* **2010**, *43*, 1588.
[17] C. M. A. Brett, G. Inzelt, V. Kertesz, *Anal. Chim. Acta* **1999**, *385*, 119.
[18] A. A. Karyakin, E. E. Karyakina, W. Schuhmann, H. L. Schmidt, S. D. Varfolomeyev, *Electroanalysis* **1994**, *6*, 821.
[19] M. M. Barsan, E. M. Pinto, C. M. A. Brett, *Electrochim. Acta* **2008**, *53*, 3973.
[20] J. Wang, Y. H. Lin, L. Chen, *Analyst* **1993**, *118*, 277.
[21] I. L. de Mattos, K. A. Shiraishi, A. D. Braz, J. R. Fernandes, *Quim. Nova* **2003**, *26*, 373.
[22] J. H. Park, I. H. Cho, S. W. Chang, *J. Environ. Sci. Health Part B, Pestic. Contam. Agric. Wastes* **2006**, *41*, 109.
[23] E. Bakker, M. Telting-Diaz, *Anal. Chem.* **2002**, *74*, 2781.
[24] R. C. Pena, J. C. M. Gamboa, T. Paixao, M. Bertotti, *Microchim. Acta* **2009**, *166*, 277.
[25] M. S. Lin, T. F. Tseng, W. C. Shih, *Analyst* **1998**, *123*, 159.
[26] Q. J. Chi, S. J. Dong, *Anal. Chim. Acta* **1995**, *310*, 429.
[27] A. A. Karyakin, E. E. Karyakina, L. Gorton, *Talanta* **1996**, *43*, 1597.
[28] A. A. Karyakin, E. E. Karyakina, L. Gorton, *J. Electroanal. Chem.* **1998**, *456*, 97.
[29] A. A. Karyakin, E. E. Karyakina, L. Gorton, *Anal. Chem.* **2000**, *72*, 1720.
[30] K. S. Tseng, L. C. Chen, K. C. Ho, *Sens. Actuator, B, Chem.* **2005**, *108*, 738.
[31] A. A. Karyakin, E. A. Puganova, I. A. Budashov, I. N. Kurochkin, E. E. Karyakina, V. A. Levchenko, V. N. Matveyenko, S. D. Varfolomeyev, *Anal. Chem.* **2004**, *76*, 474.
[32] F. Ricci, C. Goncalves, A. Amine, L. Gorton, G. Palleschi, D. Moscone, *Electroanalysis* **2003**, *15*, 1204.
[33] M. E. Ghica, C. M. A. Brett, *J. Electroanal. Chem.* **2009**, *629*, 35.
[34] R. C. Carvalho, C. Gouveia-Caridade, C. M. A. Brett, *Anal. Bioanal. Chem.* **2010**, *398*, 1675.
[35] S. J. Yao, J. H. Xu, Y. Wang, X. X. Chen, Y. X. Xu, S. S. Hu, *Anal. Chim. Acta* **2006**, *557*, 78.
[36] L. Zhang, Z. Fang, Y. H. Ni, G. C. Zhao, *Int. J. Electrochem. Sci.* **2009**, *4*, 407.
[37] W. Jia, M. Guo, Z. Zheng, T. Yu, Y. Wang, E. G. Rodriguez, Y. Lei, *Electroanalysis* **2008**, *20*, 2153.
[38] H. Razmi, A. Taghvimi, *Int. J. Electrochem. Sci.* **2010**, *5*, 751.
[39] F. L. Qu, M. H. Yang, J. H. Jiang, K. J. Feng, G. L. Shen, R. Q. Yu, *Electrochem. Commun.* **2007**, *9*, 2596.