

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec



Influence of the different carbon nanotubes on the development of electrochemical sensors for bisphenol A



Lorena Athie Goulart, Fernando Cruz de Moraes, Lucia Helena Mascaro *

Departamento de Química, Universidade Federal de São Carlos, C.P. 676, 13565-905 São Carlos, SP, Brazil

A R T I C L E I N F O

ABSTRACT

Article history: Received 7 July 2015 Received in revised form 8 September 2015 Accepted 18 September 2015 Available online 21 September 2015

Keywords: Acid treatment Bisphenol A Multi-walled carbon nanotubes Electrochemical sensor

1. Introduction

Carbon nanotubes (CNTs) have intrinsic characteristics, such as structural, mechanical, electronic, chemical and thermal stability, high resistance, elasticity, high surface area and good electrical conductivity [1,2]. All these properties make the CNTs a special material to be used in electrochemical devices. Several studies have focussed on the CNT synthesis, purification, suspension, filling and surface functionalisation [3]. Depending on the CNT synthesis methods, the CNTs may be produced as single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) [4,5]. Some properties of CNTs can be improved from the functionalisation of this material as an acid pretreatment. The treatment causes changes in the CNT morphologies, thus decreasing the size and opening the blocked ends of the nanotubes. Also, it was shown that the functionalisation steps can increase the number of defects (denoted as break-bones) in the structure of the CNT sidewall. In addition, the CNT treatment can cause the appearance of oxygenated functional groups on the CNT edge planes [6].

Most of the structural and morphologic modifications, as previously cited, are due to the treatment of the CNTs in the presence of a solution of an individual oxidant agent or a mixture of concentrated strong mineral acids. Under soft conditions, as with the functionalisation with a nitric acid solution, the decrease in the size of the tubes can be controlled and minimised. In this condition, the chemical modification is confined mostly to the opening tube edge plans and the formation of functional groups on the defect sites along the sidewalls [7]. On the

Different methods of functionalisation and the influence of the multi-walled carbon nanotube sizes were investigated on the bisphenol A electrochemical determination. Samples with diameters of 20 to 170 nm were functionalised in HNO_3 5.0 mol L^{-1} and a concentrated sulphonitric solution. The morphological characterisations before and after acid treatment were carried out by scanning electron microscopy and cyclic voltammetry. The size and acid treatment affected the oxidation of bisphenol A. The multi-walled carbon nanotubes with a 20–40 nm diameter improved the method sensitivity and achieved a detection limit for determination of bisphenol A at 84.0 nmol L^{-1} . © 2015 Elsevier B.V. All rights reserved.

other point of view, the use of a concentrated mixture of oxidant acids can lead to dramatic changes in the CNT morphology. It was reported that this kind of acid functionalisation promotes a sharp decrease of the tube diameter and unblock the CNT ends and the high incorporation of several functional groups such as hydroxyl, carboxyl, epoxide and other oxygenated species [8].

Besides the acid treatment, another important factor that influences the properties of CNTs is size, since the diameters of nanotubes directly affect the microstructure on the surface of CNTs and electrocatalytic activity [9]. One example is the determination of quercetin using CNTs with different diameters. Sensors fabricated with MWCNTs untreated with an average diameter of 50 nm were used in the amperometric detection of quercetin and the detection limit was 0.66 µmol L^{-1} [10]. In contrast, a sensor produced with MWCNTs and with an average diameter of 22.5 nm yielded a detection limit at 0.20 µmol L^{-1} [11]. The decrease in the CNT diameter caused an increase in the sensor sensitivity at the determination of quercetin.

In the other report, the synergistic effect of the diameter and CNTfunctionalisation step can also be observed in the determination of quercetin. In this report, sensors were fabricated with CNTs with diameters of 15 nm and 20 nm and treated in two different conditions, i.e., sulphonitric solution and a mixture containing concentrated nitric acid and perchlorate acid. The sensor fabricated with CNTs with 15 nm diameter and treated in a sulphonitric solution exhibited a detection limit at 4.9 nmol L^{-1} . Instead, the sensor based on CNTs with a diameter of 20 nm and functionalised in the acid mixture allowed a detection limit of 19.0 nmol L^{-1} [12,13]. These results presented that the efficiency of the sensors modified with CNTs can be enhanced using CNTs with smaller diameters and functionalised in vigorous conditions.

^{*} Corresponding author.

E-mail addresses: lorenaathie@hotmail.com (LA. Goulart), fcmoraes@hotmail.com (F.C. de Moraes), lmascaro@ufscar.br (L.H. Mascaro).

Due to the potentiality of the CNTs in electrochemical device production, this material has been extensively used for electrocatalysis and electroanalysis, including the sensitive determination of several species such as metals [14,15], pharmaceutical products [16], neurotransmitters [17,18,19], pesticides [20], hormones [21], dyes [22,23] and endocrine disruptors [24,25]. On the other hand, it is well established that there is a direct correlation with the type, size and pretreatment of the CNTs and their performance as an electrochemical sensor. However there are very few works in which it has a study of the effect of the functionalisation and the size of the CNT in the response of this material as an electrochemical sensor. It is noteworthy that despite a large number of articles on the CNT based electrochemical sensors, which show the LOD values, LOQ, sensitivity and linearity range, often do not mention the dimensions of this material or the acid treatment performed. Considering what has been described above, this study focussed on the influence of the size and type of the functionalisation step of the CNTs and their application on the sensitive determination of bisphenol A (BPA), which is an environmental target molecule.

2. Experimental

2.1. Chemicals and solutions

Samples of the MWCNTs1 (purity of 90%, length 5.0–9.0 µm, diameter 110–170 nm) were obtained from Sigma-Aldrich, and MWCNTs2 (purity of 95%, length 5–15 µm, diameter 20–40 nm) were obtained from Shenzhen Nanotech Port Co., Ltd., China. Sulphuric acid was obtained from Chemis; nitric acid was obtained from Synth and BPA was obtained from Sigma-Aldrich. All other chemicals were of analytical grade and used without further purification. 0.1 mol L^{-1} of a phosphate buffer solution (PBS – pH 7.0) was prepared using NaH₂PO₄ and Na₂HPO₄, and the pH was adjusted with NaOH. All solutions were prepared with de-ionised water (~18.2 MΩ).

2.2. Apparatus and procedure

Electrochemical measurements were carried out using an Autolab Type PGSTAT30 (Eco Chemie, Utrecht, Netherlands) potentiostat/ galvanostat coupled to NOVA software (Eco Chemie). The electrochemical cell was assembled with a conventional three-electrode system: a glassy carbon electrode (GC with area at 0.2 cm²) modified with treated and untreated MWCNTs as a working electrode, an Ag/ AgCl (KCl 3.0 mol L^{-1}) as a reference electrode and platinum as a counter electrode. All electrochemical measurements were performed in 1.0×10^{-4} mol L⁻¹ BPA in a pH 7.0 PBS solution at a controlled temperature at 25 °C. Cyclic voltammetry (CV) experiments were carried out in a potential range that varied from +0.2 V to +1.0 V and with a scan rate at 50 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) data were obtained using FRA2 software (Eco Chemie, The Netherlands) in a frequency range from 10 kHz to 10 mHz and an amplitude of 10 mV, with 10 data points per frequency decade. Measurements were carried out under open circuit potential (OCP) conditions in 0.1 mol L^{-1} PBS pH 7.0 containing 1.0 mmol L^{-1} BPA. The determination of BPA was carried out using differential pulse voltammetry (DPV) with a scan rate of 10 mV s⁻¹, amplitude at 100 mV and step potential at 2 mV. The potential was varied from + 0.2 V to + 1.0 V for BPA determination. The analytical characteristics were obtained from the addition of volumes of BPA standard solutions, and the detection limit (LOD) was calculated according to the IUPAC recommendation [26].

The morphologies of the MWCNT samples were examined using a field-emission gun scanning electron microscopy (FEG-SEM), recorded with a FEG-Zeiss model Supra 35VP (Zeiss, Germany), equipped with a higher-resolution secondary electron detector (in-lens detector) and operating at 6.0 kV and a point-to-point resolution of 3.8 nm. Samples were prepared by dropping MWCNT suspension on a glassy carbon plate. The films were dried for 12 h.

2.3. MWCNTfunctionalisation

The MWCNTs1 and MWCNTs2 were functionalised in a 5.0 mol L^{-1} of a HNO₃ solution and concentrated sulphonitric solution, which consisted a mixture of HNO₃/H₂SO₄ (3:1 by volume). For the MWCNT functionalisation, 100 mg of MWCNTs was mixed with 50 mL of HNO₃ solution. This mixture was stirred for 12 h at room temperature and was subsequently filtrated, continuously washed using purified water and dried in an oven for 12 h at 70 °C. The same procedure was performed for the functionalisation of MWCNTs with a concentrated sulphonitric solution.

2.4. Preparation of GC/MWCNTs

Prior to modification, the surface of the glassy carbon (GC) electrode surface was polished with alumina slurries $(0.3 \,\mu\text{m})$, rinsed thoroughly with double-distilled water, sonicated for 5 min in ethanol and 5 min in water and air-dried. Afterwards, the GC electrode was electrochemically cleaned in 0.1 mol L^{-1} pH 7.0 PBS with a subsequent application of anodic potential at +1.5 V during 60 s, followed by an application of cathodic potential at -1.5 V during 60 s. Then, 50 cyclic voltammograms were performed in a range of potential varying from -1.0 V to +1.0 V to obtain reproducible and stable voltammetric behaviour. For the sensor preparation, first, 1.0 mg of MWCNTs was suspended in 1.0 mL of dimethylformamide (DMF). The suspension was dispersed using ultrasonic stirring for 1 h. Then, an aliquot of 10 µL of the suspension was placed as a droplet on the GC electrode surface, and the solvent was then evaporated at room temperature. DMF was used because it was found to be more compatible than other solvents (e.g., ethanol, acetone) given the hydrophobic nature of the GC surface, and which led to a more homogeneous film.

3. Results and discussion

3.1. Characterisation of MWCNTs

The morphologies of the CNT samples (MWCNTs1 and MWCNTs2) were evaluated using FEG-SEM microscopies before and after the functionalisation step. Fig. 1A displays an image of the untreated MWCNTs1, in which it can be observed that the tubes have an average diameter of 150 nm with an average length of 5.0 µm. In addition, it is clearly observed that the CNTs presented caps on the sidewalls and in the tube ends. The same observation can be seen in the MWCNTs2 presented in Fig. 1D. However, the CNTs presented low values in the dimensions (diameter average at 48 nm) compared with the MWCNTs1. This differential in the CNT size is due to the type of synthesis method and the manufacturer [27]. Comparing the effect of acid treatment on the MWCNTs1 and the functionalisation using a nitric acid solution (Fig. 1B) promotes a 30% decrease in the CNT diameter (100 nm) compared with the pristine CNTs (MWCNTs1 - Fig. 1A). Also, it was observed in this slight treatment that the CNT ends were completely unblocked. However, using the concentrated sulphonitric functionalisation, it was presented in Fig. 1C that the tube ends were completely unblocked and the CNT sidewalls were flaked, thus leading to a large number of defects. In addition, this strong treatment decreased the CNT diameter to 70 nm.

The same behaviour of the removal of amorphous carbon caps in the end and tube sidewalls was observed for the MWCNTs2. Also, the effects of the treatment, nitric acid and sulphonitric solution allowed a decrease of the CNT average diameters at 35 nm (Fig. 1E) and 20 nm (Fig. 1F), respectively. It is clearly observed that the strong acid functionalisation using the sulphonitric solution promoted the most changes in the CNT samples. However, we emphasise that the source of the CNTs is more important than the pretreatment step. This statement can be seen when Fig. 1C and F are compared. For electrochemical sensors, the nature of the electrode material is primordial. It is sought as a nanostructured material with large surface area and electrocatalytic properties. Then,



Fig. 1. FEG-SEM micrographs for: (A) MWCNT1 untreated, (B) MWCNT1 treated with HNO₃ solution (5.0 mol L⁻¹), (C) MWCNT1 treated with a concentrated solution of 3HNO₃:1H₂SO₄; (D) MWCNT2 untreated, (E) MWCNT2 treated with HNO₃ solution (5.0 mol L⁻¹), and (F) MWCNT2 treated with concentrated solution of 3HNO₃:1H₂SO₄.

the structural changes, such as the breaking of the edge plans and anchoring of carboxylate functional groups, remarkably improved the electrocatalytic performance and conductivity of CNTs [28,29]. In this sense, the MWCNTs2 pretreated in a sulphonitric solution, displayed in Fig. 1F, become an interesting material to be used in sensor development.

3.2. Effect of the different MWCNTs on the BPA electrooxidation process

The electrocatalytic activity of different MWCNT samples was demonstrated by comparison using BPA oxidation peak potential $(E_{\rm pa})$ and oxidation current peak $(I_{\rm pa})$ obtained by cyclic voltammograms in 0.1 mol L⁻¹ PBS (pH 7.0) containing 1.0×10^{-4} mol L⁻¹ BPA (figure in Supplementary information). Fig. 2 presented the

variation of the I_{pa} and E_{pa} as a function of different materials used in the BPA electrooxidation. There are no significant changes in the I_{pa} and response of the bare GC electrodes, untreated CNTs and the sensor fabricated with MWCNTs1. However, the sensor fabricated with MWCNTs2 functionalised exhibited a sharp increase in the BPA current peak oxidation. The increase in the I_{pa} is due to the changes in the CNT structure, which leads to an increase of the electroactive area. In comparison, the sensor prepared with MWCNTs2 treated in a sulphonitric solution archived a current peak value at 33 μ A, which is almost 3.5-times higher than the untreated MWCNTs2 electrode.

Regarding the $E_{\rm pa}$ variation, the sensor with untreated MWCNTs1 presented a slight shift in the potential value for more negative values when compared with the bare GC electrode. In addition, due to the increase of the functional groups on the edge planes of the CNTs, the



Fig. 2. Plot of oxidation peak potential and oxidation peak current obtained by cyclic voltammograms of $1.0 \times 10^{-4} \text{ mol } \text{L}^{-1}$ BPA in 0.1 mol L⁻¹ PBS (pH 7.0) to different electrodes.

functionalised MWCNTs1 continuously shifted the potential for cathodic direction. However, when the MWCNTs1 sulphonitric treatment sensor response was compared with the untreated MWCNTs2 sensor, it was observed that the functionalisation step promotes the shift for more negative potential values. In contrast, for the MWCNTs2 sensors, the effect of functionalisation promoted a great shift in the E_{pa} for more negative values. This behaviour is a function of the increase of the amount of oxygenated functional groups and the decrease of the CNT dimensions, which lead to an increase of the electroactive surface area. In addition, it was reported that the functionalisation step allowed the increase of the number of edge plans that are completely linked to the electrocatalytic properties [25,30,31]. The increase in the number of edge plans promotes a faster charge-transfer rate that shows electrocatalytic behaviour. Experimentally, this effect can be seen by the shift in the potential values, as much of the literature reports [32,33].

In order to evaluate the best results for different CNT sources (MWCNTs1 and MWCNTs2) treated in sulphonitric solutions, CV experiments were carried out in 0.1 mol L⁻¹ PBS (pH 7.0) containing 1.0×10^{-4} mol L⁻¹ BPA. Fig. 3A presented the cyclic voltammograms for the sensors (a) bare GC, (b) GC/MWCNTs1 and (c) GC/MWCNTs2. A single electrochemical process was observed in all scans. This peak is attributed to an irreversible oxidation of the hydroxyl group present in the aromatic ring of the BPA to form phenoxenium ions, which is a kind of phenoxy radical [34]. Comparing these results, the GC/MWCNTs2 sensor shifted 0.10 V in the oxidation potential of BPA to a less positive value when compared with the bare GC (+0.66 V), and it shifted 0.05 V compared with GC/MWCNTs1 sensor. Additionally, the oxidation on the catalytic, presented in the MWCNTs2 treated surface, showed a 5-fold increase in the current peak compared with bare GC and a 3-fold increase in the current peak compared with GC/MWCNTs1. The low dimensions of the MWCNTs2 added to the effect of the functionalisation in a sulphonitric solution reflect a shift in the potential value, an increase in the current peak and a well-defined oxidation peak.

The electrocatalytic effects of the CNT dimensions and functionalisation steps were also evaluated using electrochemical impedance spectroscopy. The EIS experiments allowed the charge-transfer resistance values for the sensor process to be obtained. The spectra in Fig. 3B were recorded at OCP and modelled using a modified Randles equivalent circuit, consisting of the cell resistance (R_{Ω}) in series with a parallel combination of a constant phase element (*CPE*), considered as a non-ideal capacitance of capacity (*C*) and a charge-transfer resistance (R_{ct}), with a Warburg impedance (Z_w).

After fitting the parameters presented in Fig. 3B, the R_{Ω} values were very similar for the three different sensors, i.e. the value found was close to 70 Ω . The determined capacitances of the bare GC was 9.51 µF s^{α -1}, for GC/MWCNTs1 the capacitance was 33.4 µF s^{α -1} and for GC/MWCNTs2 the CPE value was 163.0 µF s^{α -1}. Compared with the electrode prepared



Fig. 3. (A) Cyclic voltammograms of 1.0×10^{-4} mol L⁻¹ BPA in pH 7.0 PBS, (a) GC; (b) GC/MWCNTs1 (3HNO₃:1H₂SO₄); and (c) GC/MWCNT2 (3HNO₃:1H₂SO₄). Scan rate: 50 mV s⁻¹. (B) Nyquist diagrams of 1.0 mM BPA in pH 7.0 PBS solution obtained at (a) GC, GC/MWCNTs1 (3HNO₃:1H₂SO₄); (c) GC/MWCNT2 (3HNO₃:1H₂SO₄). Inset: magnified plots of (a), (b) and (c) at the high-frequency region.

with MWCNTs2, the capacitance of the MWCNTs1 the increase in the *CPE* value indicating an increase in the conductive area of the CNT surface, leading to an increase in the analytical signal (current peak). However, based on the CVs experiments displayed in Fig. 3A, shifts on the potential values for more negative values were observed. This affirmation was evaluated when the electron transfer resistance was calculated. Using the equivalent circuit previously described, R_{ct} were determined bare GC was 174 k Ω , for GC/MWCNTs1 was 63.5 k Ω , and for GC/MWCNTs2 the R_{ct} value was calculated at 3.23 k Ω . These results are in agreement with the CV experiments, in which the sensor prepared with MWCNTs2 presented an increase in the peak current, well-definition of the electrochemical process and also a shift in the potential values, demonstrating the electrocatalytic effect of the surface.

3.3. Adsorption studies

It was reported that the BPA response was effected by an adsorption process in aqueous solution [35,36]. In order to evaluate the adsorption behaviour cyclic voltammetry experiments were performed. Thus, 10 successive cyclic voltammograms were carried out in 0.1 mol L⁻¹ of PBS (pH 7.0) containing 1.0×10^{-4} mol L⁻¹ of BPA, in a potential range between + 0.1 and + 1.0 V vs. Ag/AgCl, with a scan rate of

 50 mV s^{-1} . It can be observed in Fig. 4A that the BPA oxidation process (+0.55 V) decreased after the successive scans. This behaviour is due to the formation of a film from the BPA oxidation product showing an adsorption effect.

The effect of the scan rate on the peak current responses at the GC/ MWCNT2 (3HNO₃:1H₂SO₄) sensor was also investigated. In Fig. 4B, a linear increase can be observed with the scan rate between 2.5 and 100 mV s⁻¹. As the scan rate values exceeded 50 mV s⁻¹, broadening and distortion of the peak shapes are observed, which leads to the increase of the peak current values. Also, I_{pa} was directly proportional to the scan rate over the range of 2.5–100 mV s⁻¹, as shown in the inset in Fig. 4B, which suggests an adsorption process on the modified electrode surface.

As discussed, the BPA oxidation process is accompanied by an adsorption step. Therefore, a poisoning of the electrode surface may occur and consequently reduction of the analytical signal. The influence of potential pretreatment applied was investigated after each DPV voltammogram. The potential was investigated for the following values: +0.25, 0.0, -0.25, -0.50, -0.75, and -1.0 V. Complete recovery of the original response was obtained using -0.50 V as a cleaning pretreatment potential. At more positive cleaning potentials, the peak current, I_{pa} , obtained during the following experiment begins to decrease, reaching only 25% at +0.25 V pretreatment cleaning potential. Thus, -0.50 V was chosen as the pretreatment time was also evaluated, varying from 10 to 90 s. The I_{pa} increased up to 30 s and no difference was seen for higher time



Fig. 4. (A) 10 successive cyclic voltammograms at GC/MWCNT2 (3HNO₃:1H₂SO₄) electrode, of 1.0×10^{-4} mol L⁻¹ BPA in pH 7.0 PBS, with a scan rate of 50 mV s⁻¹. (B) Linear relationship between anodic current peak and the scan rate. Inset: cyclic voltammograms for the GC/MWCNT2 (3HNO₃:1H₂SO₄) electrode in 1.0×10^{-4} mol L⁻¹ BPA in pH 7.0 PBS, at a scan rate varying from 2.5 to 100 mV s⁻¹.

values, hence 30 s was chosen as the time of pretreatment for cleaning the electrode surface.

3.4. Analytical characteristics

DPV was used to investigate the electrochemical response as a function of the BPA concentration. In this study, three sets of sensors (each set consists of three different sensors such as: bare GC, GC/MWCNTs1 and GC/MWCNTs2 — in which the CNTs were functionalised in the sulphonitric solution) were employed as the working electrodes, and their analytical responses were compared. BPA standards were used to construct the calibration curves shown in Fig. 5 with three measurements for each concentration. The inset in Fig. 5 presents the DPV signals recorded for the GC/MWCNTs2 sensor.

The analytical signals exhibited a linearity range from 2.5 to 24.3 µmol L^{-1} for bare GC ($R^2 = 0.996$). For GC/MWCNTs1, the observed linearity range was 2.5 to 29.1 µmol L^{-1} ($R^2 = 0.997$). The limits of detection (LODs) were calculated at 2.03 and 0.61 µmol L^{-1} for bare GC and GC/MWCNTs1 sensors, respectively. The detectability level was remarkably influenced by the use of MWCNTs2 treated in a sulphonitric solution. The GC/MWCNTs2 sensor ($R^2 = 0.997$) exhibited a linearity range from 4.9 to 82.5 µmol L^{-1} with a LOD estimated in 0.084 µmol L^{-1} (84.0 nmol L^{-1}). The LOD values were determined using a 3 s/slope ratio, where s is the standard deviation of the mean value for 10 voltammograms of the blank.

The effect of the low MWCNTs2 diameter added to the effect of the functionalisation in a sulphonitric solution and can be further evaluated from the values for analytical sensitivity, which were almost two times higher with GC/MWCNTs2 (31.3 μ A/ μ mol L⁻¹) than with the GC/MWCNTs1 (16.5 μ A/ μ mol L⁻¹). Compared with the bare GC (10.2 μ A/ μ mol L⁻¹), the sensor modified MWCNTs2 functionalised in a sulphonitric solution presented a 3-fold increase in sensitivity. Also, the LODs and sensitivity values were compared in a T-test at a 95% confidence level, to compare the sensors based on the different CNTs studied.

In order to evaluate the efficiency of the GC/MWCNTs2 sensor functionalised with sulphonitric, a comparison with other sensors based on carbon material modified electrodes for BPA determination was performed. The unmodified boron-doped diamond (BDD) electrode was used to monitor the concentration of BPA degradation. The BDD electrode yielded a higher LOD at 210 nmol L^{-1} [37], which is a higher value than the proposed electrode in this work (84.0 nmol L^{-1}). An



Fig. 5. Linear dependence of the DPV peak current and the concentration of BPA. (a) GC (0.2; 0.4; 0.7; 0.9; 1.4; 1.9; 2.4×10^{-5} mol L⁻¹), (b) GC/MWCNT1 (3HNO₃:1H₂SO₄) (0.2; 0.4; 0.7; 0.9; 1.4; 1.9; 2.4; 2.9×10^{-5} mol L⁻¹), (c) GC/MWCNT2 (3HNO₃:1H₂SO₄) (0.4; 1.4; 1.9; 2.4; 2.9; 3.3; 4.3; 5.6; 8.2 × 10⁻⁵ mol L⁻¹). Inset: DPVs of different concentrations of BPA at the GC/MWCNT2 (3HNO₃:1H₂SO₄) electrode (a) 0.4, (b) 1.4, (c) 1.9, (d) 2.4, (e) 2.9, (f) 3.3, (g) 4.3, (h) 5.6, and (i) 8.2×10^{-5} mol L⁻¹.

electrode fabricated with MWCNT and lithium titanate $(Li_4Ti_5O_{12})$ was used at the surface modification of the GC electrode for the determination of BPA [38]. The sensor exhibited a LOD at 78.0 nmol L⁻¹. Another electroanalytical method, which exhibited a low value of LOD, was CNT carbon paste modified with cobalt phtalocyanine [39]. The sensor archived a LOD at 10.0 nmol L⁻¹. It is important to evidence that the sensor proposed here (GC/MWCNTs2) presented nanomolar detection levels, even without a modification agent. In this sense, the GC/MWCNTs2 sensor functionalised in sulphonitric solution presented efficiency in the quantitative determination of BPA.

4. Conclusion

This work showed that the dimension and type of the acid treatment of CNTs were directly influenced at the determination of BPA. The cyclic voltammetry results showed an increased analytical signal and an improvement in the electron transfer rate on the surface of the GC sensors modified with CNTs with a smaller diameter and acid functionalisation. The best results were obtained for the GC/MWCNTs2 sensor when functionalised with a sulphonitric solution. This may be related to the increased effectiveness in modifying the morphology of CNTs with the incorporation of functional groups and the greater disturbance of edge planes, compared with the functionalisation in HNO₃ solution. It can also be concluded that there is a need to clearly specify the characteristics, type and treatment of CNTs when using this material as an electrochemical sensor.

Acknowledgements

This work was supported by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) (Process: 2012/20926-2).

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.msec.2015.09.073.

References

- [1] A. Hirsch, Angew. Chem. Int. Ed. Engl. 41 (2002) 1853–1859.
- [2] F.C. Moraes, L.H. Mascaro, S.A.S. Machado, C.M.A. Brett, Electroanalysis 22 (2010) 1586–1591.
- [3] H.J. Park, M. Park, J.Y. Chang, H. Lee, Nanotechnology 19 (2008) 1-7.
- [4] D.P. Subagio, M. Srinivasan, M. Lim, T. Lim, Appl. Catal. B Environ. 95 (2010) 414–422.
- [5] E.N. Ganesh, Intern, J. Innov. Technol. Exp. Eng. 2 (2013) 311-320.
- [6] B. Kim, W.M. Sigmund, Langmuir 20 (2004) 8239–8242.
- [7] K. Balasubramanian, M. Burghard, Small 2 (2005) 180–192.
- [8] F.C. Moraes, M.F. Cabral, L.H. Mascaro, S.A.S. Machado, Surf. Sci. 605 (2011) 435–440.
 [9] C. Hu, Y. Zhang, G. Bao, Y. Zhang, M. Liu, Z.L. Wang, Chem. Phys. Lett. 418 (2005) 520–525
- [10] J. Xu, H. Zhang, G. Chen, Talanta 73 (2007) 932–937.
- [11] F. Gutiérrez, G. Ortega, J.L. Cabrera, M.D. Rubianes, G.A. Rivas, Electroanalysis 22 (2010) 2650-2657.
- [12] Q. Zhu, A.N.A. Sujari, S.A. Ghani, Sensors Actuators B 177 (2013) 103-110.
- [13] G. Jin, J. He, Z. Rui, F. Meng, Electrochim. Acta 51 (2006) 4341–4346.
- [14] X. He, Z. Qiaolia, Y. Pinga, L. Jianshe, J. Litong, Chin. J. Chem. 29 (2011) 805-812.

- [15] D. Sun, X.F. Xie, Y.P. Cai, H.J. Zhang, K.B. Wu, Anal. Chim. Acta 581 (2007) 27-31.
- [16] H. Beitollahi, I. Sheikhshoaie, Electrochim. Acta 56 (2011) 10259–10263.
- [17] R. Samba, K. Fuchsberger, I. Matiychyn, S. Epple, L. Kiesel, A. Stett, W. Schuhmann, M. Stelzle, Electroanalysis 26 (2014) 548–555.
- [18] H. Beitollahi, M. Mostafavi, Electroanalysis 26 (2014) 1090–1098.
- [19] H. Beitollahi, A. Mohadesi, S. Mohammadi, A. Akbari, Electrochim. Acta 68 (2012) 220–226.
- [20] D. Du, X. Huang, J. Cai, A. Zhang, Sensors Actuators B 127 (2007) 531-535.
- [21] B. Rezaei, S.Z.M. Zare, A.A. Ensafi, J. Braz. Chem. Soc. 22 (2011) 897–904.
- [22] S.M. Ghoreishi, M. Behpour, M. Golestaneh, Anal. Methods 3 (2011) 2842–2847.
- [23] W. Zhanga, T. Liua, X. Zheng, W. Huang, C. Wana, Colloids Surf. B: Biointerfaces 74 (2009) 28–31.
- [24] J.A. Rather, S. Pilehvar, K.D. Wael, Analyst 138 (2013) 204–210.
- [25] N.A. Martínez, S.V. Pereira, F.A. Bertolino, R.J. Schneider, G.A. Messina, J. Rab, Anal. Chim. Acta 723 (2012) 27–32.
 [26] Analytical Methods Committee Recommendations for the definition, estimation
- [26] Analytical Methods Committee, Recommendations for the definition, estimation and use of the detection limit, Analyst 112 (1987) 199–204.
- [27] R.C. Carvalho, C. Gouveia-Caridade, C.M.A. Brett, Anal. Bioanal. Chem. 398 (2010) 1675–1685.
- [28] V.M. Daskalakia, I. Fulgioneb, Z. Frontistisa, L. Rizzob, D. Mantzavinosa, Catal. Today 209 (2013) 74–78.
- [29] J. Poerschmann, U. Trommler, T. Górecki, Chemosphere 79 (2010) 975–986.
- [30] D.A.C. Brownson, C.E. Banks, Phys. Chem. Chem. Phys. 14 (2012) 8264-8281.
- [31] D.A.C. Brownson, D.K. Kampouris, C.E. Banks, Chem. Soc. Rev. 41 (2012) 6944–6976.
 [32] F.C. Moraes, T.A. Silva, I. Cesarino, S.A.S. Machado, Sensors Actuators B 177 (2013) 14–18
- [33] R. Pauliukaite, M.E. Ghica, O. Fatibello-Filho, C.M.A. Brett, Electrochim. Acta 55 (2010) 6239–6247.
- [34] Y. Qiu, H. Fan, X. Liu, S. Ai, T. Tang, R. Han, Mikrochim. Acta 171 (2010) 363–369.
- [35] A. Dehghan, M. Hossein, R. Noushin, R. Saeedi, S. Nazmara, E. Iravani, Desalin. Water Treat. 54 (2015) 84–92.
- [36] J. Bohdziewicz, G. Kamińska, Water Sci. Technol. 68 (2013) 1306–1314.
- [37] G.F. Pereira, L.S. Andrade, R.C. Rocha-Filho, N. Bocchi, S.R. Biaggio, Electrochim. Acta 82 (2012) 3–8.
- [38] W. Wang, X. Yang, Y. Gu, C. Ding, J. Wan, Ionics 21 (2015) 885–893.
- [39] H. Yin, Y. Zhou, S. Ai, J. Electroanal. Chem. 626 (2009) 80-88.

Lorena Athie Goulart received her B.Sc. degree in Chemistry from Universidade Federal de Mato Grosso, Brazil, in 2009. She completed her Technical Chemistry course from Instituto Federal de Mato Grosso, Brazil, in 2008 and her M.S. degree in Analytical from Universidade Federal de Mato Grosso, Brazil, in 2012. Actually she is a Ph.D. student at Universidade Federal de São Carlos, Brazil. Her research areas of interest include electrochemical oxidation, flavonoid, biodiesel and development of carbon nanotube and TiO₂ electrodes. She is a member of the International Society of Electrochemistry (ISE).

Fernando Cruz de Moraes received his B.Sc. degree in Chemistry from Universidade Federal de São Carlos, Brazil, in 2002. His M.S. degree in Physical Chemistry from Universidade de São Paulo, Brazil and his Ph.D. in 2010 in Physical Chemistry from Universidade Federal de São Carlos, Brazil. Actually he is a researcher at the Institute of Chemistry of São Carlos of Universidade de São Paulo. The research areas of interest are related with electroanalysis, mainly, on development and characterisation of sensors and biosensors based on carbon nanotube for electrochemical detection of biological and environmental samples. He has published 29 articles and he has more than 50 participations in conferences. He is a member of the International Society of Electrochemistry (ISE), of the Sociedad Iberoamericana de Electroquímica (SIBAE).

Lucia Helena Mascaro received her M.S. degree in 1988 and Ph.D. in 1992 in Physical Chemistry from Universidade Federal de São Carlos, in Brazil. She has been contracted in 2003 as assistant professor and in 2006 as associate professor from Universidade Federal de São Carlos, in Brazil. Her research areas of interest include conducting polymers, electroanalysis, ultra microelectrodes, analyses of pesticides, and modifications of electrode surfaces with carbon nanotubes. She has published 60 articles, 3 chapters of book and more than 150 participations in conferences. She is a member of the International Society of Electrochemistry (ISE) of the Sociedad Iberoamericana de Electroquímica (SIBAE).