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Nafion® modified-screen printed gold electrodes and their carbon nanostructuration for electrochemical sensors applications

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ABSTRACT

Screen printed electrodes are frequently used in electroanalytical applications because of their properties such as small size, low detection limit, fast response time, high reproducibility and disposable nature. On the other hand, since the discovery of carbon nanotubes there has been enormous interest in exploring and exploiting their properties, especially for their use in chemical (bio)sensors and nanoscale electronic devices. This paper reports the characterization of gold screen printed electrodes, modified with Nafion® and nanostructured with carbon nanotubes and carbon nanofibers dispersed on Nafion®. The dispersing agent and the nanostructure have a marked effect on the analytical signal that, in turn depends on the intrinsic characteristics of the analyte. Several model analytes have been employed in this study. Anionic, cationic and neutral species such as methylene blue, dopamine, iron (III) sulfate, potassium ferrycianide and urea were considered. The importance for the development of nanostructured sensors relies on the fact that depending on these factors the situation may vary from a notorious enhancement of the signal to a blocking or even decrease.

1. Introduction

Nafion® is a cationic exchange polymer that has been extensively employed as a membrane on electrode surfaces. This membrane allows conduction of cationic species and blocks anionic species from reaching the electrode surfaces [1]. The increasing popularity of Nafion® for the fabrication of modified electrodes arises from easy fabrication and many advantageous chemical and physical properties as good electrical conductivity, high partition coefficients of many redox compounds in Nafion® and good biocompatibility [2]. Nafion® film also has high chemical stability and ability to resist interferences from anions and also biological macromolecules [3–5] and therefore can minimize loss of selectivity due to anionic species [1]. A very thin film of Nafion® is ample to offer minimal obstruction to the diffusion of the analyte to the electrode surface, while at the same time preventing adsorption/desorption processes of organic species in biological fluids [6]. Nafion® polymer as an effectively permselective barrier [7–9] can circumvent the entry of anionic biological interferences. Procedures for the preparation of the modified electrodes are very convenient and fast [10]. The use of polymeric membrane Nafion® has become very attractive due to its negative charge, since foreign species such as ascorbic acid, paracetamol, uric acid, etc. are readily repelled [11–14]. The number of potential foreign species is then restricted by molecular size, permeation and/or (bio)chemical reaction. The addition of a thin Nafion® coating to the electrode surface resulted in a large increase in peak current compared to bare electrode, and the linear accumulation through the membrane allows the detection [15].

Since their discovery in 1991 [16], carbon nanotubes (CNTs) have attracted the interest of researchers belonging to different disciplines. Their physical and chemical properties make them very promising materials for their use in nanotechnology, which is reflected by the increasing number of studies published in the last years [17]. Composite materials based on solubilizing CNTs with various polymers, especially Nafion®, have been reported [18]. Because of the unique ion exchange and discriminative and biocompatible properties, Nafion® films containing various electrocatalytic materials [19] have been extensively employed for the modification of the electrode surfaces and applied for the voltammetric sensing in electrochemical sensors and biosensors. Nafion®–CNT bioelectrodes coated with an extra Nafion® membrane, eliminate interfering signals and possess enhanced storage time and performance, in comparison to the biosensors made without Nafion® and other biomaterials and/or mediators can be incorporated in the Nafion®–CNT matrix for the fabrication of useful biosensors [20]. The use of CNTs (Nafion® dispersed) for preparation of sensors have been described in the literature. However, a discussion of the effect that this dispersing agent as well as the carbon structure has on the signal of very different

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analytes (anionic, cationic and neutral electroactive species) in a comparative way has not been reported. CNTs (Nafion®-dispersed) have been employed for modification of glassy carbon electrodes for improving the detection of hydrogen peroxide [18] and, including also Pd nanoparticles, for the construction of a DNA hybridization sensor with methylene blue (MB) as indicator molecule [21]. Similarly, carbon paste electrodes were modified with CNTs dispersed in Nafion® and thionine for dopamine detection [22]. CNTs grown over silicon substrate were used for the potassium ferricyanide detection [23]. However, modification of screen-printed electrodes is very scarce, with reports on screen-printed carbon electrodes [24]. In this paper, an electrochemical characterization of nanostructured gold screen printed electrodes (AuSPEs) is made with electroactive species of different nature.

2. Material and methods

2.1. Reagents and solutions

Nafion® (perfluorinated ion-exchange resin, 5 wt. % solution in a mixture of lower aliphatic alcohols and water), methylene blue (certified by the BSC), dopamine, potassium hexacyanoferrate (III) trihydrate and boric acid were obtained from Sigma-Aldrich (St. Louis, MO, USA). Sodium hydroxide and potassium chloride as well as sulfuric (95–97% of purity), phosphoric (85%) and acetic (100%) acids were purchased from Merck (Whitehouse Station, NJ, USA). Potassium ferricyanide was obtained from Probus (Badalona, Barcelona, Spain), iron (III) sulfate from Panreac (Montplet and Esteban, Barcelona, Spain) and urea from Riser. Finally, amine functionalized multi-walled carbon nanotubes (MWCNT–NH_2) were purchased from Nanocyl (Auvelais, Belgium) and carboxylic functionalized carbon nanofibers (CNFs–COOH) were kindly provided by the company “Grupo Antolín” (Valencia, Spain). MWCNTs were produced via catalytic carbon vapor deposition (CCVD) process. They were purified to greater than 95% carbon (3100 grade) and functionalized with a Nanocyl patented process (3150 grade). Britton–Robinson buffer solutions were prepared by mixing boric, phosphoric and acetic acid (0.04 M each) and fixing the pH with NaOH. Water was purified employing a Milli-Q directQS system from Millipore.

2.2. Apparatus

Voltammetric and impedance measurements were performed with an Autolab PGSTAT 12 potentiostat (EcoChemie) interfaced to a Pentium 120 computer system and controlled by Autolab GPES and FRA software version 4.8. A JEOL 6610LV Scanning Electron Microscope (30 kV) was used to characterize bare and carbon nanostructured gold working electrodes. An Elma ultrasonic bath, a Nahita centrifuge with interchangeable car, a Mettler Toledo AB54 balance, a Crison Micro-pH 2001 pH-meter, a magnetic stirrer Asincro, a Sanyo refrigerator and a Sanyo MIR-162 incubator were also used.

2.3. Gold screen-printed electrodes

Gold screen-printed electrodes purchased from DropSens (ref. 220AT) include a traditional three-electrode system printed on the same strip. The configuration includes a gold disk (12.6 mm^2) as working electrode, a silver pseudo-reference electrode and a gold counter electrode using the same ink of the working electrode. All of them were screen-printed on a ceramic substrate ($3.4 \times 1.0 \times 0.05$ cm) and subjected to high-temperature curing. An insulating layer serves to delimit the working area and electric contacts. The production characteristics of commercial SPEs are regarded by the manufacturers as proprietary information. A specific connector supplied also by DropSens allows their connection to the potentiostat.

2.4. CNTs and CNFs dispersions

Generally, carbon nanotubes are presented in the market as a black solid powder (although recently some companies sell them in solution and even electrodes modified with solutions of carbon nanotubes [25]). Therefore, most of applications of CNTs require a pre-solubilisation step for obtaining a homogeneous suspension. There are two important factors that have to be taken into account: the ratio CNTs weight/volume of solvent and the dispersion procedure. To carry out this work an ultrasonic bath and a centrifuge with interchangeable car for 1.5 and 5 mL have been employed following the procedure of [26]. Briefly, a fixed amount of carbon nanotubes (1 mg) is dispersed in a known volume of solvent (1 or 5 mL) and subjected to cycles, two hours in the ultrasonic bath and 10 min of centrifugation. After each cycle the precipitate is discarded and the supernatant is subjected to a new cycle until finally a uniform solution is achieved. Not all the solvents are appropriate from the electroanalytical point of view and a thorough study was performed previously [27]. Attending to this, Nafion®–ethanol was employed for the dispersion of aminated CNTs. In brief, four cycles of ultrasonic bath (100%) and centrifugation (5000 rpm) were employed, discarding the supernatant after each cycle. Finally, this dispersion was diluted 1:1 with purified water.

The dispersion of carbon nanofibers can be made by simply putting a small amount of carbon nanofibers (1 mg) together with a small volume of water (1 mL) and subjecting the mixture to an ultrasonic bath for 5 min. In this particular case, water was replaced by a solution of Nafion® in ethanol, in order to compare the studies with those of CNTs.

2.5. Electrodes modification with Nafion® or carbon nanostructures

Nafion®, a sulfonated tetrafluoroethylene based copolymer is an anionic synthetic polymer with cationic exchange properties. Electrode modification with the dispersing agent (Nafion®) or electrode modification with carbon nanostructures was carried out by evaporation at room temperature of a drop of Nafion® or CNTs/CNFs dispersion deposited on the working electrode. Volumes of 2 and 5 μL were used, respectively. The electrochemical characterization was carried out scanning the potential in solutions of different electroactive species: cationic, anionic and neutral species such as methylene blue, potassium ferricyanide, urea and iron (III) sulfate.

2.6. Electrochemical characterization

2.6.1. Voltammetric characterization

Methylene blue is an organic dye that belongs to the phenothiazine family, with cationic properties. At room temperature it appears as a solid, dark green powder, which yields a blue solution when dissolved in water. The electrochemical characterization of electrodes modified with Nafion® and those nanostructured with CNTs was carried out by cyclic voltammetry, scanning the potential between $+0.2$ and -0.35 V in 40 μL drops of 2.0×10^{-5} M MB in Britton–Robinson buffer, pH 4, in order to reduce first MB to LB that in turn is oxidized again to MB.

Dopamine is a neurotransmitter produced in several areas of the brain, and also released by the hypothalamus. Its influence in neurological disorders makes its determination relevant and usually is performed electrochemically. It presents 3 pK_a: 8.9, 9.6 and 12.0, and therefore it is also a cationic molecule at pH 4. In this case, cyclic voltammograms were recorded in a 10^{-4} M dopamine solution in 0.1 M Britton–Robinson buffer, pH 4.

Iron (III) sulfate was chosen for characterization of electrodes since is multivalent cationic specie and then can be compared to results obtained for methylene blue and dopamine, with less positive charges. Cyclic voltammograms recorded from -0.4 V to $+0.6$ V on a 5.0×10^{-4} M $Fe_2(SO_4)_3$ solution in 0.1 M H_2SO_4 pH 1.

Urea or carbamide is an organic compound with two amine groups joined by a carbonyl functional group that plays an important role in the metabolism of nitrogen-containing compounds, being the main nitrogen-containing substance in the urine of mammals. Cyclic voltammograms were recorded in 1 mM urea in Britton–Robinson buffer pH 7 on bare, Nafion®-modified and CNTs nanostructured electrodes (previously modified with Nafion®) by scanning the potential from -0.1 to $+0.5$ V.

Ferricyanide is a potassium anionic salt very used for electrochemical characterization of new electrodes since it has an adequate and known electrochemical behavior. Its anionic character suggests that the behavior on Nafion® modified electrodes will be different to that observed with methylene blue. Cyclic voltammograms were then recorded by scanning the potential from -0.2 to $+0.45$ V in 3.3×10^{-4} M potassium ferricyanide solutions in Britton–Robinson buffer, pH 2.

2.6.2. Impedimetric characterization

Electrochemical impedance spectroscopy studies were made in order to characterize the electrode surface. These measurements were performed at the equilibrium potential of the $Fe(CN)_6^{-4}/Fe(CN)_6^{-3}$ couple, with a 10 mV (rms, root-mean-square) sinusoidal excitation amplitude. Solutions of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$, 5 mM in each component in 0.1 M KCl, were used.

3. Results and discussion

When an electrodic surface is going to be modified, not only the nature of the analyte has to be considered but also the modifier and the dispersing agent (in case is needed). For a nanostructuration with carbon nanotubes, the present functional group is responsible for the different behavior of nanostructured electrodes [27], showing those functionalized with amino groups an electrodic surface with notable advantages in terms of enhancement of analytical signals. Therefore, amino functionalized multi-wall carbon nanotubes (MWCNTs–NH_2) have been chosen for the studies involved in this work.

Referring to the analytes chosen for the studies, all of them present a very adequate electrochemical process, reversible in most of the cases. Some of them can be employed for the development of biosensors since they can act as detectable molecules with ability for bioconjugation. Methylene blue, dopamine, iron (III) sulfate, potassium ferricyanide and urea, a selection that includes anionic, cationic and neutral species has been considered.

When considering the electrochemical behavior on a modified electrode, the dispersing agent could have a very relevant influence, varying from no effect on the analytical signal to its enhancement or a total blocking. Therefore the signals obtained for nanostructured electrodes will be always compared to those obtained for the dispersant agent itself.

A first evaluation of the nanostructuration is made by scanning electron microscopy (SEM). With this aim, images of unmodified AuSPEs, and those modified with Nafion® and CNTs (Nafion® dispersed) were taken, as well as of the surface obtained when CNTs are added after Nafion® modification. Elements analysis was also performed. Four different images are presented in Fig. 1. When bare electrodes were considered (Fig. 1A), only Au is found in the elements analysis. The SEM image show the typical aspect of SPAuEs [28]. Particles heterogeneous in size and shape stand out and the electrodes can be considered as a random array of both recessed and inlaid microelectrodes. When Nafion® is added to modify the electrode surface (Fig. 1B), Au, C and F are found in the analysis performed and a recovered surface by the Nafion® membrane can be observed. Further addition of carbon nanotubes

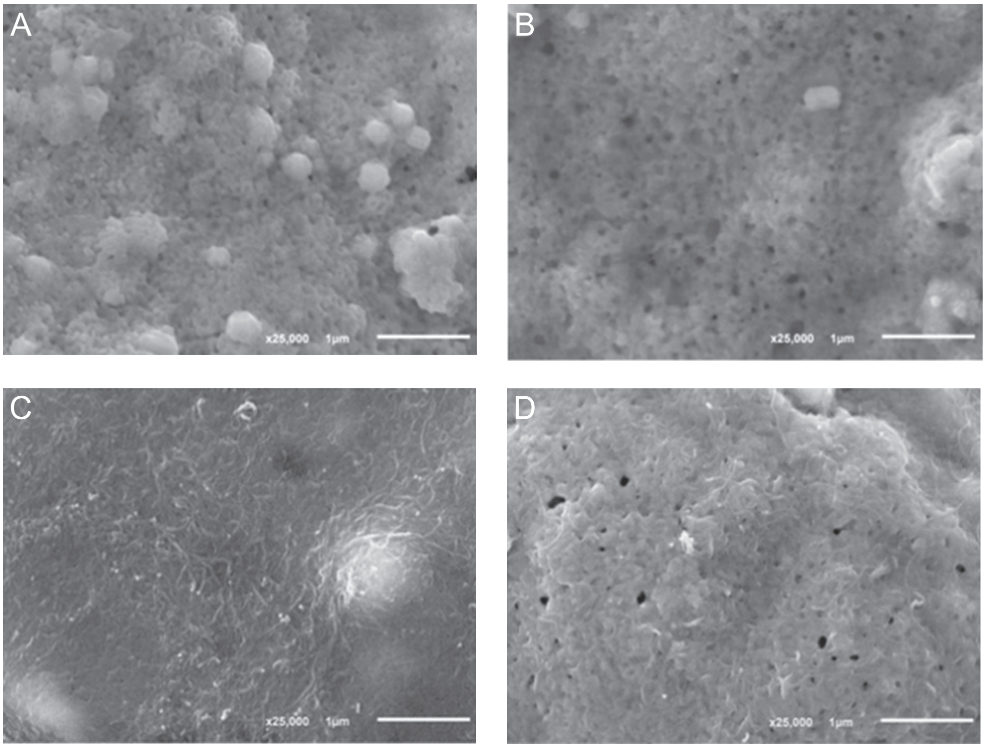

Fig. 1. SEM images for bare electrode (A), Nafion®-modified electrode (B), CNTs nanostructured Nafion®-modified electrode (C) and CNTs nanostructured electrode (D).

over this electrode surface (Fig. 1C) is the responsible to the increase of C and F in the element analysis. SEM image is observed as tangles of filamentous over the Nafion® membrane. Finally, when CNTs were dispersed in Nafion® and this solution is employed for modification of the electrode, CNTs are observed as filamentous inserted in between the membrane of Nafion® (Fig. 1D). The higher content of C and F and the lower content of Au have been found in the electrodes where CNTs were added over the Nafion®-modified electrode.

3.1. Methylene blue

Fig. 2 shows the voltammograms obtained after electrode modifications and compared with that for the bare electrode. The cyclic voltammogram recoded on the bare electrode shows a cathodic process at -0.365 ± 0.008 V corresponding to the conversion of methylene blue to leucomethylene blue (LB) in a two electron process [29]. The corresponding anodic process appears at -0.262 ± 0.005 V which means a difference of 0.103 V. In this case, low peak currents were obtained for both, the anodic (0.502 ± 0.008 μA) and cathodic (-0.768 ± 0.006 μA) processes with a ratio of $i_{\mathrm{p\ an}}/i_{\mathrm{p\ cat}}=0.65$. In contrast, when the electrode is modified with a Nafion® layer, total loss of the electrochemical response is observed. This blocking of the signal may be due to the ion exchange properties of Nafion®, so it can easily exchange positively charged ions through the film [30,31], as is the case of MB. The film generated could hinder the diffusion of the analyte so that MB signal disappears. However, when MWCNTs–NH_2 was dispersed on this agent and screen printed electrodes were modified with the dispersion, an increase in the analytical signal is obtained, what is clearly due to CNTs. If Nafion® modified electrodes (and therefore with no signal for MB) were later nanostructured with carbon nanotubes, not only the recovery of the electrochemical signal was observed but also a considerable improvement in peak currents. One possible explanation to this phenomenon is the tunneling effect of CNTs [32], a conduction model based on electrons passing, one by one, between two neighboring CNTs. However, it is difficult to distinguish between tunneling and contact between adjacent CNTs and probably both phenomena could occur. In this case, new peak intensities were 5.95 ± 0.03 and -3.828 ± 0.007 μA for anodic and cathodic process, respectively. These were very similar to those obtained for direct nanostructuration with Nafion®-dispersed CNTs. With respect to the peak potential, there is a slight shift to less positive/negative values, in the case of the anodic/cathodic peaks, respectively, indicating that oxidation and reduction become easier. They move from -0.262 ± 0.002 to -0.276 ± 0.001 V and from -0.365 ± 0.004 to -0.310 ± 0.006 V, for anodic and cathodic processes, respectively. Reversibility of the process after the nanostructuration was improved since ΔE is 34.3 mV vs. 103.3 mV of difference on bare electrodes. This is very important when electroanalytical techniques that improve sensitivity of reversible processes such as square wave or differential pulse voltammetry could be employed.

An electrochemical impedance spectroscopy study was made in order to characterize the surfaces generated. Fig. 3A shows the Nyquist plots obtained from bare and modified AuSPEs meanwhile the Fig. 3B indicates the equivalent circuit, the Randles Cell. A diffusion process is clearly observed for bare electrodes. When the electrode was modified with a Nafion® membrane, the charge-transfer resistance (R_{CT}) resulted to be 81.8 mΩ meanwhile the double-layer capacitance (C_{dl}) was 4.1 μF. AuSPE modified with a Nafion® membrane and later nanostructured with CNTs dispersed in Nafion®, showed a decrease in the value of R_{CT} (30.8 mΩ) and higher C_{dl} (9.5 μF). Finally, nanostructured AuSPEs with CNTs dispersed in Nafion® presented 1.10 mΩ (the lower resistance value) and 12.6 μF double layer capacitance. These results show that blocking with Nafion® (high resistance to charge transfer) is reversed with addition of CNTs, being the more conductive surface this nanostructured with a dispersion of CNTs in Nafion®.

In order to study the effect of the carbon nanostructures on the electrode surface, screen-printed electrodes were nanostructured with carbon nanofibers and characterized. The peak currents obtained for the cyclic voltammograms recorded are presented in the bar diagram of Fig. 4, where they are compared to those obtained for CNTs. Surprisingly, the electrodic process of MB is only present on bare electrodes. After blocking the electrode with Nafion®, the addition of CNFs (that are Nafion® dispersed) does not allow recovery of the signal. It seems that a different structure does not allow forming an electron pathway, either by tunneling or by direct contact between nanostructures happened with MWCNTs. This demonstrates the importance in the choice of the nanostructure for electrode modification.

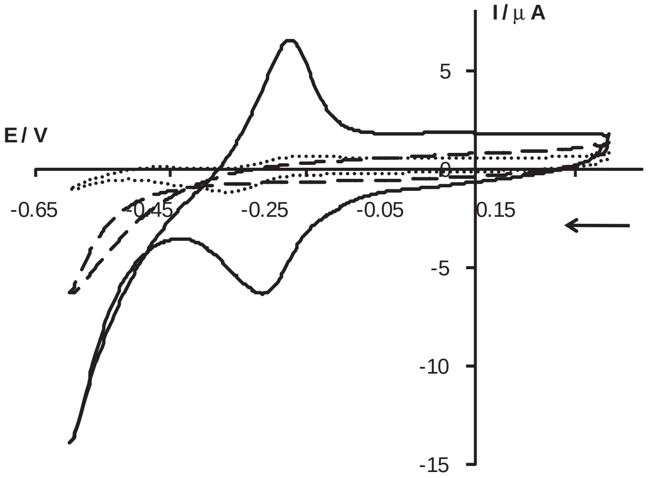

Fig. 2. Cyclic voltammograms (ν=0.1 Vs^{-1}) for 2.0×10^{-5} M methylene blue in Britton–Robinson buffer pH 4.0 on bare (…), Nafion®-modified (- - -) and MWCNT-NH_2 nanostructured (––) electrodes.

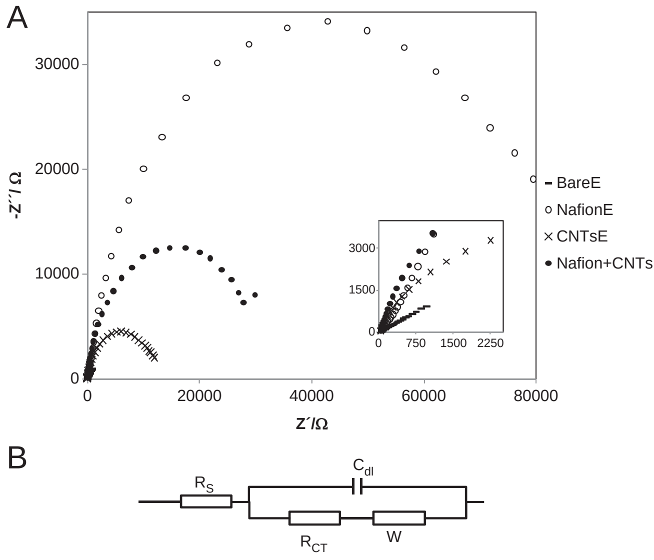

Fig. 3. Nyquist plots obtained from bare and modified electrodes (A) and the equivalent circuit corresponding to the Randles Cell, with R_s (electrolyte solution resistance), R_{CT} (specific charge transfer resistance), W (Warburg resistance) and C_{dl} (double layer capacitance).

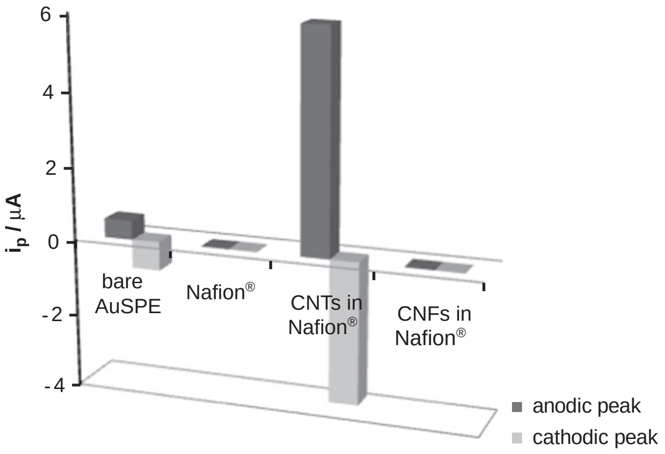

Fig. 4. Bars diagram corresponding to the peak current of cyclic voltammograms (ν=0.1 Vs^{-1}) for 2.0×10^{-5} M in Britton–Robinson buffer pH 4.0 on bare, Nafion®-modified and MWCNT–NH_2 or CNF–COOH nanostructured electrodes.

3.2. Dopamine

Cyclic voltammograms obtained are shown in Fig. 5A. Apart from the considerable increase in the peak currents for both processes an important enhancement of the reversibility is observed. Intensities obtained were 2.319 ± 0.002 and -1.181 ± 0.002 µA on bare electrodes, 18.66 ± 0.03 and -27.3 ± 0.1 µA on Nafion® modified electrodes and 85.90 ± 0.03 and -85.42 ± 0.04 µA on CNTs nanostructured electrodes, for anodic and cathodic peaks, respectively. The ratios of the peak currents are respectively 1.96 ± 0.02, 0.7 ± 0.1 and 1.01 ± 0.04. The modification of the electrodes supposed also a slight movement in the peak potential towards less positive values on anodic (0.381 ± 0.004, 0.2943 ± 0.0007 and 0.2005 ± 0.0005 V, on bare, Nafion®-modified and CNTs-nanostructured electrodes, respectively) and cathodic peaks (0.0403 ± 0.0006, 0.116 ± 0.004 and 0.166 ± 0.007 V similarly). This implies that processes are favoured since they occur at lower potentials. The value of ΔE was 341 ± 16, 179 ± 9 and 34.3 ± 0.9 mV respectively.

Again it is observed the recovery of the behavior of electroactive species on nanostructured surfaces with carbon nanotubes in presence of Nafion®, as is the case with the other cationic species, methylene blue. However, in this case there is not blocking with a Nafion® membrane, probably due to the small size of dopamine.

3.3. Iron (III) sulfate

Cyclic voltammograms recorded are presented in Fig. 5B. In this case, modification with Nafion® increases the signal that in turn, is enhanced again with CNTs (from 7.497 ± 0.002 to 12.02 ± 0.04 and 24.67 ± 0.06 µA for the anodic process and from -2.593 ± 0.001 to -7.51 ± 0.04 and -24.11 ± 0.03 µA for the anodic process). From the ratio between peak currents (anodic and cathodic) it can be deduced that a more reversible process is obtained for nanostructured electrodes (1.02 vs. 1.60 for Nafion® modified and 2.89 for bare electrodes). This can be observed also after calculation of ΔE: 222.0 ± 0.7, 125.9 ± 0.4 and 116.7 ± 0.3 mV for AuSPE, Nafion®–AuSPE and CNTs–AuSPE respectively. Therefore, the electrochemical process of the iron specie is enhanced in the presence of CNTs, as occurs with the other species. However, in this case not only a blocking of the electrode for Nafion®-modified electrodes is not observed (as happened for MB) but an enhancement of the signal is produced.

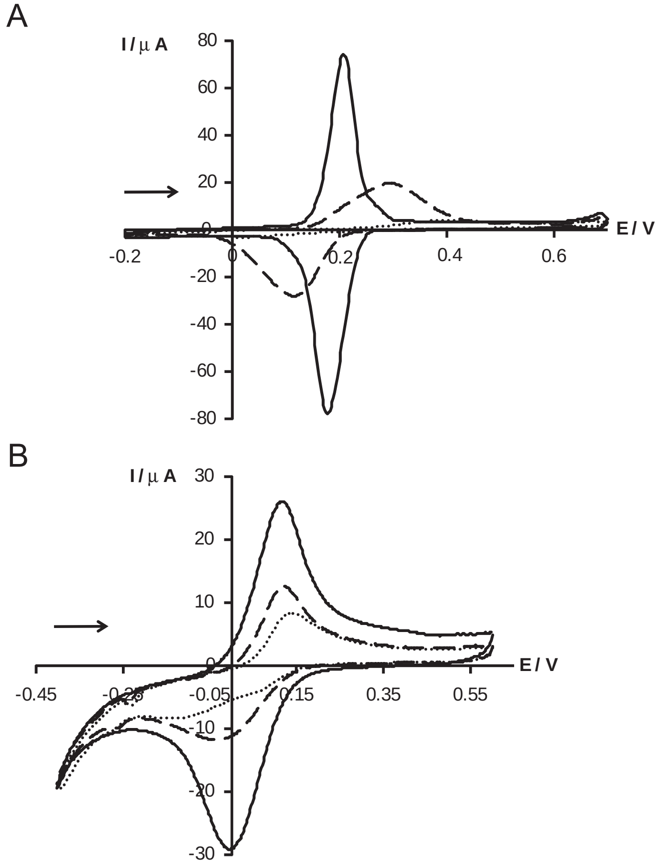

Fig. 5. Cyclic voltammograms (ν=0.1 Vs^{-1}) for 10^{-4} M dopamine in Britton–Robinson buffer pH 2.0 (A) and 5.0×10^{-4} M $Fe_2(SO_4)_3$ in 0.1 M H_2SO_4 (B) on bare (…), Nafion®-modified (- - -) and MWCNT-NH_2 nanostructured (—) electrodes.

3.4. Urea

Since in previous sections the analytical signal of cationic species was evaluated in CNTs modified electrodes and results were different (enhancement or not of the electrochemical signal compared to this obtained on bare electrodes), a different model neutral analyte was chosen: urea. On bare electrode (AuSPE), processes appear at -0.3516 ± 0.0003 and -0.7658 ± 0.0001 V meanwhile on Nafion® modified electrode the signal does not disappear but moves to more negative values: -0.3958 ± 0.0005 and -0.8231 ± 0.0004 V, for anodic and cathodic peaks respectively, indicating that the reduction process is not favored. Finally, on nanostructured electrodes (CNTs–AuSPE), the values of peak potentials move to -0.3653 (more similar to bare electrode) and -0.9306 V, indicating an increase in the irreversibility of the process. Concerning to the intensities, these are shown in the bar diagram of Fig. 6, for anodic and cathodic processes. In this case, the signal is not completely blocked with Nafion® and the nanostructuration with CNTs only produces a considerable increase in the anodic process.

3.5. Potassium ferricyanide

Cyclic voltammograms are reported on Fig. 7, with the aim of comparing the results with those of MB. The highest intensities were obtained for bare electrodes, 10.58 ± 0.04 and -10.08 ± 0.02 µA for anodic and cathodic peaks respectively where an almost reversible process is observed (ΔE of 66.4 mV and a ratio of peak intensities of 1.05). The signal is almost blocked for Nafion® modified electrodes, probably due to the anionic nature of the molecule. When the characterization was made on modified electrodes first with

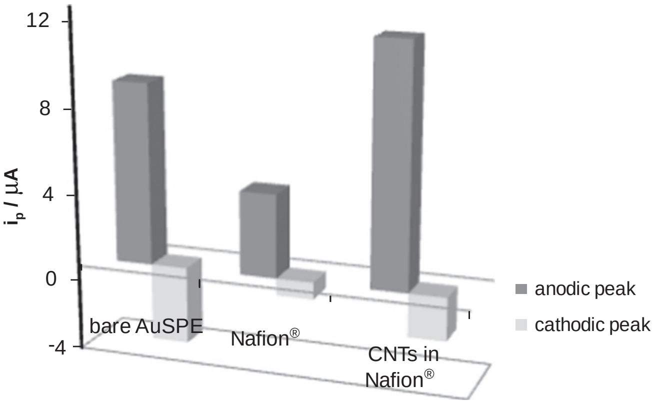

Fig. 6. Bars diagram corresponding to the peak current of cyclic voltammograms (v=0.1 Vs^{-1}) for 1mM urea in Britton–Robinson buffer pH 7.0 on bare, Nafion®-modified and MWCNT–NH_2 nanostructured electrodes.

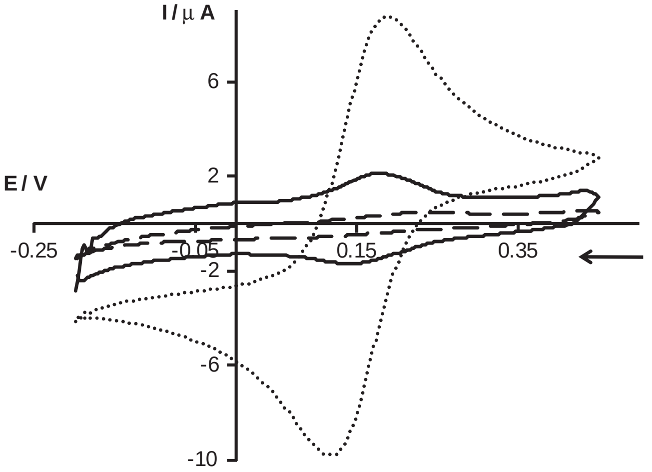

Fig. 7. Cyclic voltammograms (ν=0.1 Vs^{-1}) for 3.3×10^{-4} M potassium ferricyanide in Britton–Robinson buffer pH 2.0 on bare (…), Nafion®-modified (- - -) and MWCNT-NH_2 nanostructured (—) electrodes.

Nafion® and later nanostructured with CNTs, the signal is 1.161 ± 0.003 and -0.799 ± 0.001 µA for anodic and cathodic peaks, respectively. Not significant movements in potential peaks were observed. They remained at around 0.19 (anodic) and 0.13 V (cathodic). These results indicate that the Nafion® membrane formed offers some repulsion on the ferricyanide anion specie as the highest intensities are obtained for the unmodified electrode, while carbon nanotubes are responsible for the slight increase in intensity shown.

4. Conclusions

Electrode nanostructuration is an important alternative for increasing the analytical signal of molecules of interest. However, three important elements have to be taken into account: the dispersant agent, the nanostructure and the analyte. In order to study their influences, the behavior of different model analytes, cationic, neutral or anionic was evaluated. Very different situations could be found and the effect of the electrode modification on the signals can vary drastically. It is very significant the total blocking of the signal in the case of methylene blue on a Nafion® modified AuSPE meanwhile this is increased for the case of dopamine or $Fe_2(SO_4)_3$, also cationic species which have less size or more positive charge. Addition of CNTs on the Nafion® layer produces recovery of the signal (that is greatly enhanced) in the case of MB but also an increase in the signal of dopamine or $Fe_2(SO_4)_3$. The effect of CNTs is therefore very suitable from the analytical point of view, since it produces high increases of the signal but also enhancement of the reversibility, which it is very clear in the case of dopamine and allows sensitivity improvement by using electroanalytical techniques that magnify reversible processes. This behavior can be considered almost general but depending on the analyte the opposite is true. This is the case of potassium ferricyanide in which the peak current were higher on bare electrodes. This may be due to its anionic properties and repulsion on the surface modified with Nafion®. The nanostructuration with CNTs produces higher signal but it does not overcome those obtained on bare electrodes. On the other hand, neutral species, such as urea, suffers a decrease in peak currents on electrodes modified with Nafion® and a slight increase on CNTs nanostructured electrodes. On the other hand, the type of nanostructure is also important. In this work MWCNTs–NH_2 produced the recovery of a blocked signal probably due to a tunneling effect and an increase in the connectivity. However, this effect is not observed when carbon nanofibres are deposited on the Nafion® layer.

Acknowledgments

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