

Effect of the Dispersing Agent on the Electrochemical Response of Glassy Carbon Electrodes Modified with Dispersions of Carbon Nanotubes

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Abstract

The electrochemical response of a glassy carbon electrode modified with carbon nanotubes (CNT) dispersed in two solvents, water and DMF, and two polymers, chitosan and Nafion is reported. The films were homogeneous when the dispersing agent was water or DMF. In the case of polymers, the surfaces present areas with different density of CNTs. A more sensitive electrochemical response was obtained when CNTs are dispersed in the solvents. In the case of CNT dispersed with polymers, the nature of the polymer demonstrated to be a critical parameter not only for dispersing the nanotubes but also for the electrochemical activity of the resulting electrodes.

Keywords: Carbon nanotubes, Scanning electrochemical microscopy, Chitosan, Nafion, Hydrogen peroxide sensors

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1 Introduction

Carbon nanotubes (CNTs), one of the allotropic forms of carbon, have emerged as a new promising class of electronic materials due to their unique properties [1,2]. They consist of cylindrical graphene sheets rolled up delimiting a hollow tube with nanometer diameter and different conductivity depending on the structure [1–3]. The exceptional electronic properties of CNT have made possible their successful application as electrode material, providing a new and interesting alternative to design electrochemical sensors [4–7].

One of the characteristics of CNTs is their tendency to form bundles due to their important inter-tube hydrophobic interactions. In fact, pristine CNTs are very hard to dissolve in usual solvents [8], making its application for the development of CNT-based electrochemical (bio)sensors difficult. Therefore, to make the application in electrochemical (bio)sensing platforms possible, the surface of CNTs can be functionalized either covalently or noncovalently. Among these alternatives, the noncovalent strategy is the most interesting since the sp^2 -conjugated can be conserved avoiding the disruption of the unique electronic characteristics of CNTs. Thus, we can find several examples in the literature describing the use of CNTs dispersed in surfactants [9,10], solvents [11], polymers [11–17], ionic liquids [18] and mineral oil [19], among others.

Chitosan (CHIT) has been largely used to obtain electrochemical sensors for different analytes. In 2007, we reported the study of two chemical treatments to improve the stability of a film of CNT dispersed in CHIT at GCE for the adsorption of DNA [20]. The best electrochemical response was obtained by using glutaraldehyde as covalent cross-linker compared to the use of NaOH as ionic stabilizer. The effectiveness of different CHIT crosslinking agents has been also reported [21,22]. Nafion has been successfully used for the dispersion of CNT and further preparation of electrochemical sensors and biosensors [23,24].

In 2008 Jara-Ulloa et al. [25] reported that the electrochemical response of a 4-nitroimidazole derivative at a glassy carbon electrode (GCE) modified with CNTs dispersed in water was more sensitive than the one obtained when using GCE modified with CNT dispersed in dimethylformamide (DMF). On the other hand, Kruusenberg et al. reported a small effect of the surfactant used to disperse the CNT on the oxygen electroreduction at GCE modified with CNT dispersed in different surfactants [26].

Despite the large number of publications focused on the application of CNT for developing electrochemical (bio)sensors [27,28], just few reports are devoted to evaluate the influence of the dispersing agent on the topographic characteristic and the relationship with the electrochemical response of the resulting modified electrodes.

Studies to determine the possible relationship(s) that may exist between surface characteristics and the dispersibility of CNTs are still currently a subject of interest, as it is demonstrated for the number of publications and reviews about this topic [29].

In the present work we discuss the influence of the agent used to disperse multiwalled carbon nanotubes on the electrochemical response of GCE modified with the resulting dispersions and its relation with the characteristic of the dispersion. We have evaluated two classes of dispersing agents, solvents (DMF and water) and polymers (Nafion and CHIT). The electrodes were characterized by scanning electron microscopy (SEM), cyclic voltammetry; scanning electrochemical microscopy (SECM) and amperometry.

2 Experimental

2.1 Reagents

Chitosan (CHIT, medium molecular weight, Cat. N° 44887-7) and ferrocene methanol (FcOH) were purchased from Sigma; Nafion (Naf) and glutaraldehyde (GTA) were received from Aldrich; dimethylformamide (DMF) and hydrogen peroxide were acquired from Merck. Oxidized multiwall carbon nanotubes (MWCNT, purity >95%, 1–5 μm length and (30 ± 15) nm diameter, Cat. N° PD30L1-5-COOH) were obtained from NanoLab (USA). Other chemicals were reagent grade and used without further purification. Ultrapure water (18 M Ωcm) from a Millipore-MilliQ system was used for preparing all the solutions.

2.2 Apparatus

Scanning Electrochemical Microscopy (SECM), Cyclic Voltammetry (CV), and Amperometry measurements were performed with CHI 900, CHI 440 and CHI 604C potentiostats, respectively (CH Instruments Inc., USA). Scanning electron microscopy (SEM) images were obtained with a Field Emission Gun Scanning Electron Microscope (FE-SEM, Zeiss, SIGMA model).

For SECM measurements a $\sim 10 \mu\text{m}$ diameter home-made carbon fiber electrode served as SECM tip, while GCE of 3 mm diameter (Model CHI104, CH Instruments) were used as SECM substrate. A platinum wire and Ag/AgCl, 3 M NaCl (BAS, Model RE-5B) were used as counter and reference electrodes, respectively. All potentials are referred to that reference electrode. A magnetic stirrer provided the convective transport when necessary. All the experiments were performed at room temperature.

2.3 Modification of Glassy Carbon Electrodes

2.3.1 Preparation of the Dispersions

The dispersions were obtained by mixing 1.0 mg of MWCNTs with 1.0 mL of ultrapure water (CNT-H₂O),

DMF (CNT-DMF), 2.0% v/v Naf prepared in ethanol (CNT-Naf) or 1.0% w/v CHIT prepared in 1.0% v/v acetic acid solution (CNT-CHIT), followed by sonication for 15 min at room temperature.

2.3.2 Preparation of Glassy Carbon Electrodes Modified with MWCNT

Previous the modification, GCE were polished with alumina slurries of 0.30 and 0.05 μm for 2 min each and copiously rinsed with MQ water.

For the modification, 5 μL of the corresponding dispersion were dropped on the top of polished GCE followed by the evaporation of the solvent at 50 °C for 15 min. In the case of GCE modified with CNT-CHIT, once evaporated the solvent, the electrode was immersed in a 3.0% v/v GTA solution for 2 seconds and then washed with ultrapure water for 10 seconds [24].

For comparison, GCE were modified with CHIT (GCE/CHIT) and Naf (GCE/Naf) by dropping 5 μL of 1.0% w/v CHIT (in 1.0% v/v acetic acid solution) or 2.0% v/v Naf (in ethanol) on the top of polished GCEs followed by exposure to air at 50 °C for 15 min. Once dry, GCE/CHIT was immersed in a 3.0% v/v GTA solution for 2 seconds and washed with ultrapure water for 10 seconds.

2.4 Procedures

2.4.1 SECM Experiments

A feedback mode was selected as operation mode [30,31]. The experiments were carried out in 0.100 mol dm⁻³ phosphate buffer solution pH 7.40 using 5.0×10^{-4} mol dm⁻³ FcOH as redox mediator. The tip potential (E_T) was held at 0.500 V to produce the oxidation of FcOH, while the substrate potential (E_s) was kept at 0.000 V to permit the feedback between the electrodes. Part of the dispersion (no more than 1/3 of the surface) was removed from the modified GCE and an approach curve was conducted on the exposed surface at a tip scan rate of 0.5 $\mu\text{m/s}$. The tip was stopped when i_T reached 1.25 times $i_{T,\infty}$ ($i_{T,\infty} = 4naFDC$, where F is the Faraday constant, n is the number of electrons transferred in the tip reaction, D is the diffusion coefficient of electroactive species, C is the bulk concentration of the redox mediator and “ a ” is the tip radius). According to the theoretical curve that describes the dependence of i_T with the distance between the tip and the substrate (d), 1.25 $i_{T,\infty}$ corresponds to a d of $\sim 10 \mu\text{m}$ for a tip of 5 μm radius [32].

2.4.2 Cyclic Voltammetry Experiments

The cyclic voltammetric experiments were performed using a 0.100 mol dm⁻³ Britton–Robinson buffer pH 7.40 as supporting electrolyte and 1.0×10^{-3} mol dm⁻³ FcOH as probe. The experiments were conducted varying the scan rate between 0.010 and 0.300 V s⁻¹.

2.4.3 Amperometric Experiments

Amperometric measurements were conducted in a stirred 0.100 mol dm⁻³ Britton–Robinson buffer solution pH 7.40 by applying the desired working potential and allowing the transient currents to decay to a steady-state value prior to the addition of H₂O₂ and subsequent current monitoring.

3 Results and Discussion

3.1 Microscopic Characterization of GCE Modified with Dispersed CNT

3.1.1 Scanning Electron Microscopy

Figure 1 depicts the SEM images for GCE modified with CNTs dispersed in different media: (A) H₂O, (B) DMF, (C) CHIT and (D) Naf. The electrodes modified with CNTs dispersed in H₂O and DMF show a homogeneous

distribution of the nanotubes and a rough aspect. On the contrary, the images of the glassy carbon surfaces modified with CNTs dispersed in CHIT and Naf show an irregular coverage with a pattern of islands with high content of CNTs. Images obtained at higher magnification show a laxer distribution of CNTs at glassy carbon surfaces when the CNTs were dispersed in water and DMF instead of polymers (Inset).

3.1.2 Scanning Electrochemical Microscopy

SECM experiments were performed in order to obtain information about the topography and electroactivity of GCE modified with CNT dispersions. Figure 2A and B display SECM images obtained at GCE modified with 1.0 mg/mL CNT dispersed in (A) H₂O and (B) DMF. At GCE/CNT-H₂O the surface is homogeneous from the electrochemical point of view, with a normalized current 2.5 times higher than $I_{T,\infty}$. Considering that at bare GCE the normalized current is 1.25 $I_{T,\infty}$, it is clear that the

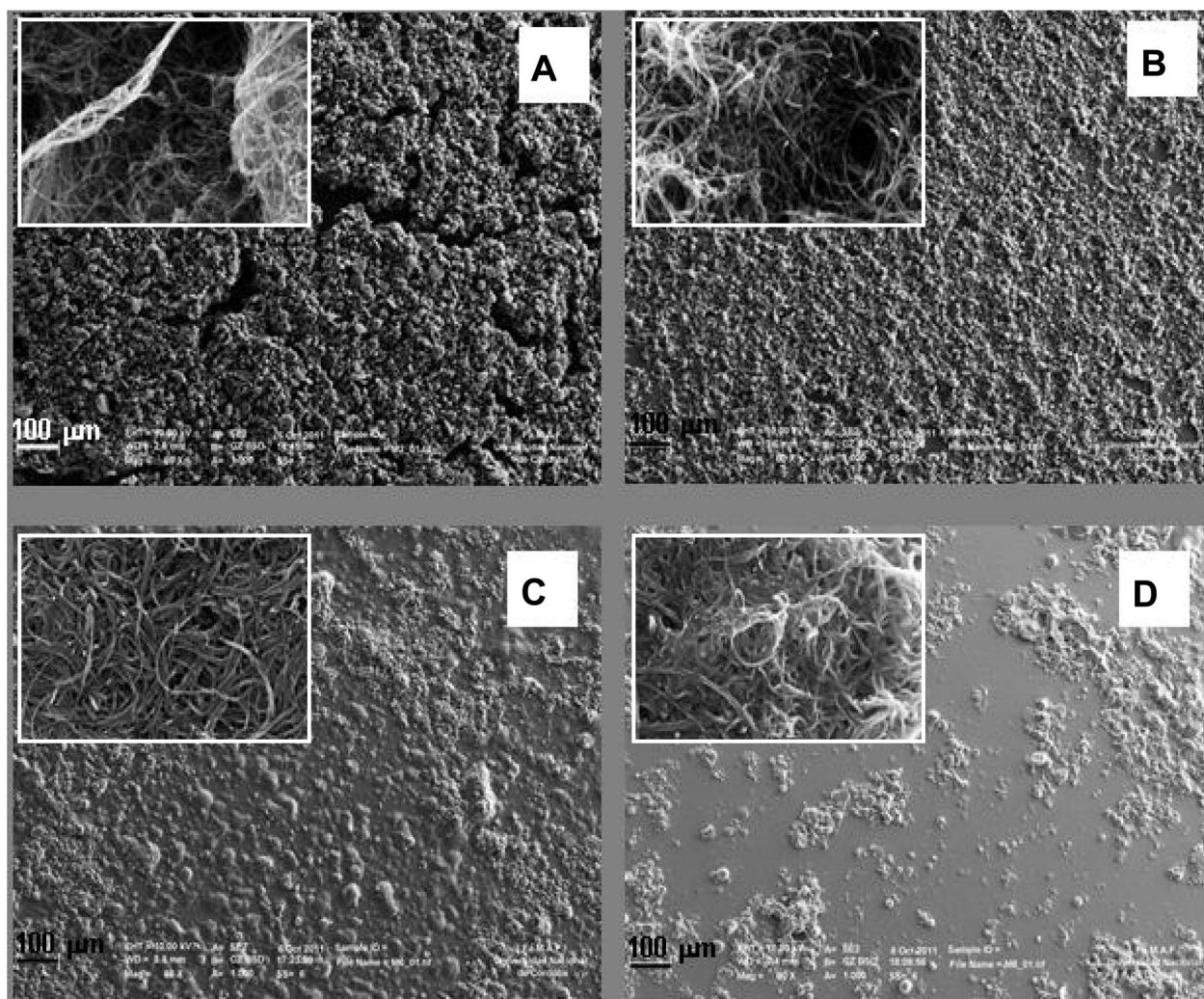


Fig. 1. SEM pictures obtained at GCE modified with 1.0 mg/mL of CNT dispersed in A) H₂O; B) DMF; C) CHIT and D) Naf. SE2 detector at 10.0 kV of acceleration voltage, and 80× of magnification. Insets: Detector InLens at 5.00 kV acceleration voltage, magnification: 25000×.

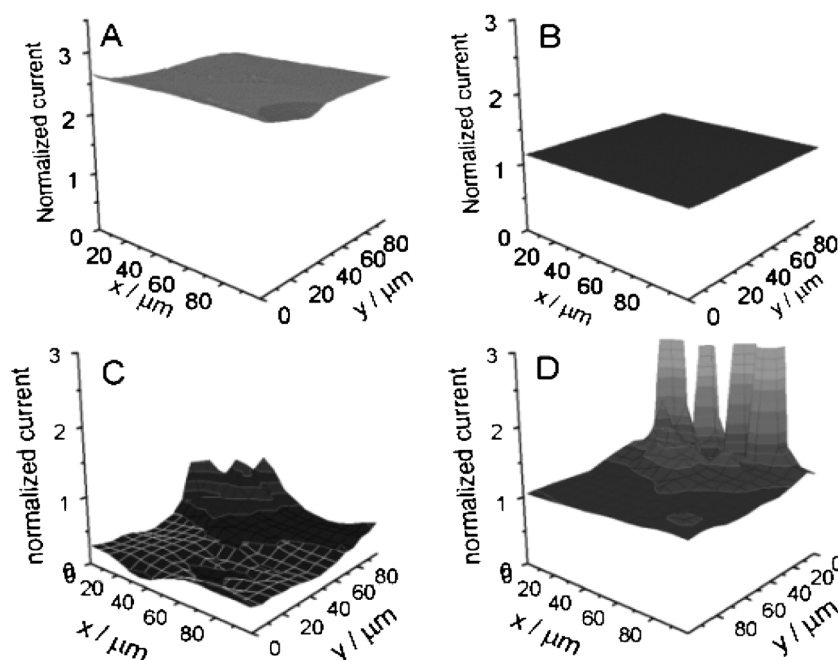


Fig. 2. SECM surface-plot images of A) GCE/CNT-H₂O (B) GCE/CNT-DMF (C) GCE/CNT-CHIT and (D) GCE/CNT-Naf modified with 1.0 mg/mL of CNT dispersion. Experimental conditions: FcOH 5.0×10^{-4} mol dm⁻³ in 0.050 mol dm⁻³ phosphate buffer pH 7.40. Image parameters: 1 μ m/s tip scan, $E_T = 0.500$ V and $E_S = 0.000$ V.

presence of CNTs largely improves the electroactivity of the resulting electrode. Compared to GCE/CNT-H₂O, the surface of GCE/CNT-DMF is more homogeneous, although it is less electroactive (normalized current of $1.15 I_{T,\infty}$). The normalized current of FcOH at GCE modified with DMF without CNTs is $1.0 I_{T,\infty}$ (Supporting Information, Figure 1SI). These results indicate that, even when DMF dispersed efficiently the CNTs, this solvent produce a blocking effect that is partially reversed for the CNTs. For both dispersing agents, the homogeneous responses observed are in agreement with the topography evidenced in the SEM images.

Figure 2C and D display SECM images obtained for GCE modified with CNT dispersed in Naf (C) and CHIT (D), respectively. In both cases there are regions with different electroactivity due to the existence of areas with dissimilar amount of CNT, in agreement with the images obtained by SEM. The approach curves show profiles that go from a positive feedback behavior in the areas with high normalized currents, (high amount of CNT), to curves with negative feedback behavior at zones with small normalized currents, (very low or null quantity of CNT), demonstrating the difference in electroactivity of these different regions (Supporting Information, Figure 2SI).

To estimate the contribution of the polymer itself in the global electrochemical behavior of GCE/CNT-polymers, we also evaluate SECM images obtained with GCE modified with Naf and CHIT in the absence of CNTs (Figure 3).

In both cases homogeneous surfaces are observed, although the normalized current decreases to $1.00 I_{T,\infty}$ for GCE/Naf and even more drastically for GCE/CHIT (down to 0.30), demonstrating that the blocking effect produced by the layer of CHIT is considerably more pronounced than that of Naf. However, is important to remark that, even when both polymers decrease the electroactivity of GCE, this effect is reversed by the presence of CNTs.

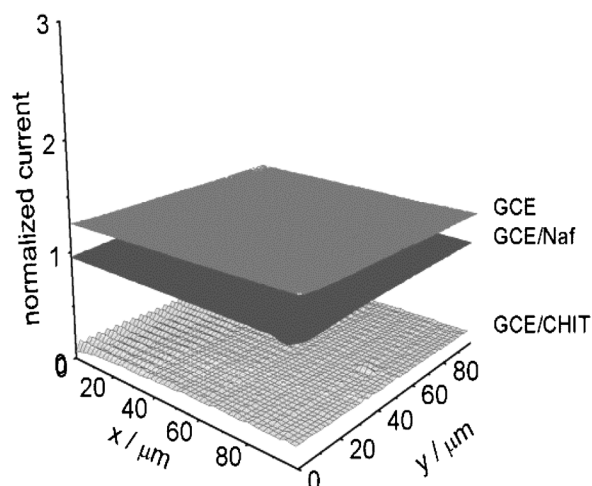


Fig. 3. SECM surface-plot images of GCE, GCE/Naf and GCE/CHIT. Experimental conditions: FcOH 5.0×10^{-4} mol dm⁻³ in 0.050 mol dm⁻³ phosphate buffer pH 7.40. Image parameters: 1 μ m/s tip scan, $E_T = 0.500$ V and $E_S = 0.000$ V.

3.2 Electrochemical Characterization of GCE Modified with Dispersed CNT

3.2.1 FcOH Electrochemical Response

Figure 4 shows the cyclic voltammetric response of FcOH at GCE modified with 1.0 mg/mL of (A) CNT-H₂O, (B) CNT-DMF, (C) CNT-CHIT, and (D) CNT-Naf (solid lines). The response obtained at bare glassy carbon is also included for comparison (dash-dotted line). Table 1 summarizes the voltammetric parameters for the electrooxidation of FcOH at the different electrodes.

The voltammograms of FcOH at GCE modified with CNTs dispersed in the solvents are very similar; with broad and asymmetrically distorted oxidation peaks that indicate a strong reactant adsorption [33]. To obtain the electrochemical parameters, the voltammograms were treated using a Gaussian fit and the corresponding curves are shown in the Supporting Information (Figure 3 SI, red line). The oxidation peak potentials (E_{pa}), its associated currents (i_{pa}) and the peak potential separation (ΔE_p) are similar for both electrodes. Compared to GCE, i_{pa} are higher (8.2 and 7.0 times for GCE/CNT-H₂O and GCE/CNT-DMF, respectively), ratio (i_{pc}/i_{pa}) are closer to 1.0 and ΔE_p are smaller.

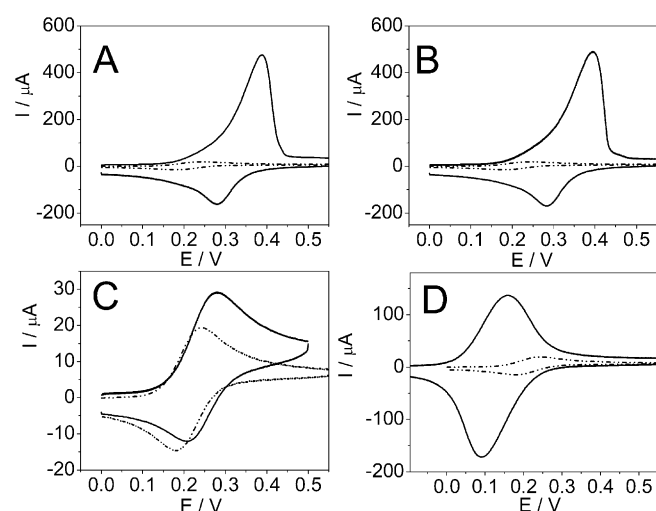


Fig. 4. Cyclic voltammograms of 0.100 mol dm⁻³ FcOH obtained at 0.100 V s⁻¹ on GCE (dotted lines) and GCE modified (solid lines) with 1.0 mg/mL of CNTs dispersed in: (A) H₂O (B) DMF (C) CHIT and (D) Naf. Experimental conditions: Britton–Robinson buffer solution pH 7.40.

At GCE/CNT-CHIT, E_{pa} shift to more positive values, i_{pa} is smaller, and i_{pc}/i_{pa} largely decreases to 0.41 (see Table 1). At variance with this behavior, at GCE/CNT-Naf, there is an important shifting of E_{pa} to less positive values as well as an important increase of i_{pc}/i_{pa} . In addition, i_{pa} and i_{pc} are 7.0 and 13.6 times higher than at GCE, respectively. This particular increase in the reduction currents confirms a facilitated adsorption of ferricinium cation at the negatively charged surface of CNT-Naf. Experiments performed at different scan rates demonstrate that i_{pa} of FcOH depends linearly on the scan rate, as it is expected for a surface controlled process (not shown).

In order to evaluate the contribution of CNTs and polymer to the global response, we performed cyclic voltammograms at GCE modified only with Naf and CHIT (without CNTs). The corresponding voltammograms are shown in Supporting Information (Figure 4 SI) and the parameters are summarized in Table 1. At GCE/CHIT, the oxidation and reduction processes occur at almost the same potentials than at GCE/CNT-CHIT, although i_{pa} is smaller due to the absence of CNTs. These effects corroborate the blocking action of the cationic polymer towards the reduction of ferricinium, in agreement with the results obtained by SECM. On the contrary, at GCE/Naf, the peaks are broad and there is an important shift in E_{pa} to less positive values as well as an important increase of i_{pc}/i_{pa} . These effects confirm a facilitated adsorption of ferricinium cation at the negatively charged surface of Nafion that was also observed at GCE/CNT-Naf.

In summary, the FcOH oxidation currents increase at all the surfaces modified with CNTs either dispersed in solvents or polymers. In the case of water and DMF, most of the CNT deposited on the GCE are accessible once the solvent is evaporated; the exposed hydrophobic surface facilitates the adsorption of FcOH producing a large increment of its oxidation currents. The behavior of FcOH at GCE modified with CNT-polymers mainly depends on the charge of the polymer. Therefore, the global behavior of GCEs modified with CNTs represent a balance between two contributions, the effectiveness for dispersing CNTs by the solvent or the polymer, and the influence of the dispersing agent on the electrochemical response of the probe.

Table 1. Electrochemical parameters determined from cyclic voltammetry of FcOH.

Surface	E_{pa} (V)	ΔE_p (V)	i_{pa} (μA)	i_{pc}/i_{pa}
GCE	0.243	0.063	19.3	0.76
GCE/CNT-H ₂ O	0.318	0.043	159	1.06
GCE/CNT-DMF	0.322	0.041	135	1.19
GCE/CNT-CHIT	0.278	0.069	29.0	0.41
GCE/CNT-Naf	0.159	0.069	136	1.27
GCE/CHIT	0.273	0.067	12.9	0.24
GCE/Naf	0.145	0.058	16.4	1.85

3.2.2 Hydrogen Peroxide Electrochemical Response

There is great interest in developing sensitive sensors for hydrogen peroxide quantification since it is a common product of several enzymatic reactions. Tkac and Ruzgas in 2006 evaluate the effect of different solvents and the polymers CHIT and Naf as dispersing agent of pristine single walled carbon nanotubes. These CNTs are by nature hydrophobic and, in consequence, long sonication times, in the scale of hours, are necessary to disperse them. The effectiveness of the dispersing agent was indirectly evaluated through the analysis of hydrogen peroxide electrochemical response at potentials as high as +900 mV [11].

Considering the importance of hydrogen peroxide and taking into account that it is a neutral molecule, it was used as redox marker to evaluate the amperometric behavior of the different platforms. The amperometric experiments were performed with GCE modified with dispersions containing 4.0 mg/mL CNTs.

Figure 5 shows amperometric recordings at 0.700 V for successive additions of $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ hydrogen peroxide at GCE (a) and at GCE modified with 4.0 mg/mL of CNT dispersed with H_2O (b), DMF (c), CHIT (d), and Naf (e). The corresponding calibration plots are shown in the inset. A well-resolved and fast signal is obtained for all the electrodes. The sensitivity depends on the electrode surface modification, in agreement with the results previously shown. The highest sensitivities correspond to GCE/CNT- H_2O and GCE/CNT-DMF, being these values 10.4 and $8.4 \mu\text{A mM}^{-1}$, respectively. The sensitivities obtained at GCE/CNT-CHIT and GCE/CNT-Naf are

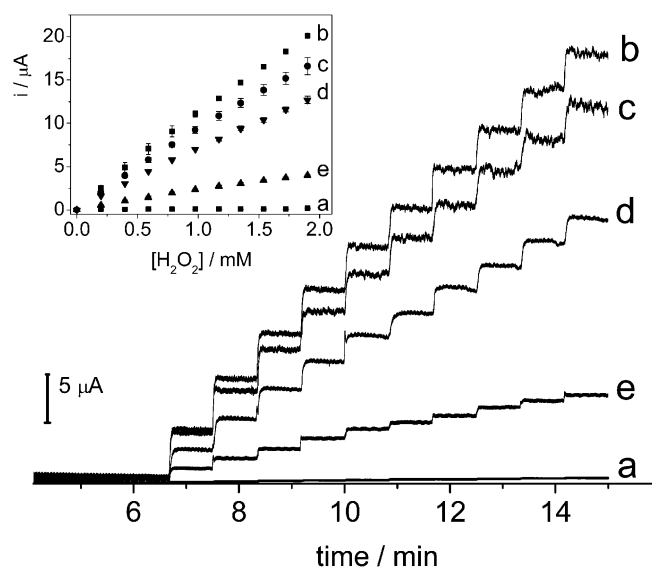


Fig. 5. Amperometric response of $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ hydrogen peroxide obtained at 0.700 V at (a) GCE (b) GCE/CNT- H_2O (c) GCE/CNT-DMF (d) GCE/CNT-CHIT and (e) GCE/CNT-Naf prepared with 4.0 mg/mL of CNTs. Inset: Corresponding calibration plots. Supporting electrolyte: $0.100 \text{ mol dm}^{-3}$ Britton–Robinson buffer pH 7.4.

$6.4 \mu\text{A mM}^{-1}$ and $2.1 \mu\text{A mM}^{-1}$, respectively. Even the lowest sensitivity is 42 times higher than the one obtained under similar conditions for GCE ($0.05 \mu\text{A mM}^{-1}$). It is important to remark that the hydrophilic properties of the acid treated-MWCNT used here facilitate its dispersion in the polar solvents water and DMF with the consequent increase of sensitivity towards hydrogen peroxide. The same tendency was observed by Tkac and Ruzgas for dispersions prepared by sonication for 17 h, optimal conditions for hydrophobic SWCNTs [11].

Hydrodynamic voltammograms obtained for $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ hydrogen peroxide at GCE and GCE modified with 4.0 mg/mL of CNT dispersed in H_2O , DMF, CHIT, and Naf were also performed (Supporting Information, Figure 5 SI). The overvoltages for the oxidation and reduction of hydrogen peroxide largely decrease and the associated currents increase at all the GCE modified with CNTs, clearly indicating the catalytic activity of CNTs towards oxidation and reduction of hydrogen peroxide.

4 Conclusions

The comparison of the electrochemical behavior of GCE modified with MWCNT dispersed in different media reveals the strong effect of the dispersing agent on the electroactivity of the modified electrode. The response can be easily understood if separating the dispersing agents in two groups, solvents (DMF and water) and polymers (CHIT and Naf). From the point of view of the ability to disperse CNT and thereby generate homogeneous surfaces on GCE, the solvents showed a much higher capacity as was revealed by SEM and SECM studies. Therefore, GCE/CNT-solvents allow obtaining the highest analytical signals towards H_2O_2 . In the case of the polymers, despite the analytical sensitivity is between 2 and 5 fold lower than those obtained at GCE/CNT-solvents, is important to remark that the polymers confer to the electrodes additional characteristics mainly related to their charge, that make possible a differentiated response selecting the adequate probe.

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