



# Waterborne carbon nanotube ink for the preparation of electrodes with applications in electrocatalysis and enzymatic biosensing

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## ABSTRACT

Conductive inks with optimal properties for amperometric sensor fabrication are key materials for low cost and high performance electrodes printed on flexible substrates. In this work, electrodes made with a carbon nanotube (CNT) waterborne ink were prepared and characterized. The electrodes showed mechanical stability and electrocatalytic behavior. Moreover, they were used for the immobilization of horseradish peroxidase (HRP) and their performance as enzymatic biosensors was assessed. Oxygen plasma treatment was used to generate carboxylic functionalities for enzyme immobilization. Its effect on the electrodes was investigated in order to optimize their performance. These electrodes were fabricated with an ink that provides a potentially simple route for roll-to-roll biosensor printing.

## 1. Introduction

Carbon nanotubes (CNTs) have attracted the attention of the research community during the last decades due to their mechanical and electrical properties. They are composed of rolled graphene sheets that can act as electrical conductors or semiconductors depending on their chirality forming a functional 1D nanomaterial. They have been employed in combination with polymers and surfactants for the preparation of different conductive and semiconductor composite materials and inks [1–12]. These preparations have been used for the fabrication of flexible electronic components employing different printing techniques such as 3D printing [13], screen printing [7], gravure [14] and inkjet printing [2–4,8,11], among others.

CNT dispersions have been widely used for coating on paper and porous substrates. Once the coating dries, CNTs entangle within the pores of the substrate and surfactants can be washed away leaving CNTs attached to the substrate [12]. However, when coating nonporous substrates, the use of binders for ink formulation is mandatory and these cannot be removed without removing the CNTs. Binders and surfactants wrap around CNTs stabilizing suspensions and forming a homogenous film after drying. They also reduce the contact between CNTs, diminishing the conductivity of coatings. Some post-treatment of dried films for improving conductivity have been reported [6], but they involve the use of strong acids, which limits its application due to

practical and environmental considerations.

With respect to their applications in the field of sensors, CNT inks have been employed as active materials in both physical [8] and chemical sensors. Especially, they have been used for the fabrication of conductimetric [5], amperometric [1,7], and potentiometric [12] sensors. Regarding amperometric sensors, their electrochemical properties have been recently reviewed [15,16]. It has been claimed that the use of CNT-based materials as working electrodes enhances electron transfer kinetics and enlarges the electroactive area [15–21]. Moreover, CNTs provide mechanical stability allowing the fabrication of electrodes on flexible materials.

Carbon electrodes printed onto flexible substrates are suitable for biosensor fabrication due to their low cost and ease for the immobilization of biomolecules. Different approaches have been used to produce functionalized carbon electrodes, such as the addition of microparticles [22] and nanoparticles [23,24], and the use of oxygen plasma treatment. Oxygen plasma promotes the formation of carboxylic functionalities on the surface of the electrode [25] which can be used for protein immobilization [26]. Plasma treatment can be also scaled to roll-to-roll production, thus allowing the functionalization of electrodes directly coupled to the printing process. So far, CNT ink-based amperometric electrodes have been fabricated as thick films and multilayers: CNT-based screen printing ink [7,27], CNT ink deposited by drop casting onto screen printed carbon or metal electrodes [28], and

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multilayers of CNT ink by inkjet printing [29–31]. A single printed layer of CNT ink, which could be used as amperometric electrodes, would be suitable for scaling up the production of such electrodes. Although a CNT ink has already been used for the fabrication of large-area thin film electrodes by rod coating [6], the application of such electrodes as amperometric biosensor has not been reported previously.

Considering the above, the aim of this work was to develop a waterborne CNT ink, which could adhere to flexible plastic substrates, could be applied in a single layer, modified for protein immobilization and used for the preparation of amperometric enzymatic electrodes.

## 2. Materials and methods

All chemicals were of reagent grade and used without further purification. Multiwalled carbon nanotubes (NC70000, Nanocyl, Belgium), acrylic-styrene resin (Joncryl® 617, made in Argentina under license of Johnson Polymer) and polyvinylpyrrolidone (PVP K30, Anedra, Argentina) were used for the preparation of the ink.

CNT were dispersed in water using PVP as dispersant with mechanical agitation and a probe-type sonicator. Then, the acrylic-styrene resin was added to the dispersion with mechanical agitation. The CNT concentration in the ink used in this work was 2.5% w/w. For the electrochemical measurements, except for the enzymatic electrodes, Pt rotating disk electrodes of 5 mm in diameter were spin coated with the CNT ink. For the enzymatic electrodes, Valox™ plastic substrates were spin coated or rod coated using a Mayer rod coating bar N°1 (wet film thickness 6 μm) and treated with oxygen plasma. Oxygen plasma treatment of these electrodes was performed using a Diener Plasma System (Diener Electronic GmbH + Co. KG, Germany) with an oxygen pressure of 1 mbar. Treatment time was varied between 5 and 180 s. Horseradish peroxidase (HRP) was immobilized onto the electrode surface using the carbodiimide coupling method as described elsewhere [26,32]. Plasma treated electrodes were put in contact for 30 min with a solution formed by mixing 100 μl of 0.1 M 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and 10 μl of 25 mM *N*-hydroxysuccinimide (NHS). After rinsing, they were incubated for 2 h with 50 μl of a 2.5 U μl<sup>-1</sup> HRP in 0.1 M phosphate buffer of pH 7.0. Finally, the electrodes were rinsed and ready to be used.

A conventional three-electrode electrochemical cell was used for the electrochemical measurements. A Pt foil with an area of 5 cm<sup>2</sup> was used as counter electrode and a silver/silver chloride electrode (Ag|AgCl|1 M KCl) was used as reference electrode. Electrochemical measurements were carried out using a Teq4 potentiostat (NanoTeq, Argentina). Sheet resistance of films was measured using the 4-point probe method with a Jandel manual 4-point probe connected to a Keithley 4200-SCS semiconductor characterization system (Tektronix, USA).

Scanning Electron Microscopy (SEM) images were obtained with a FEI Quanta 250 cold field emission scanning electron microscope operated at 30 kV.

## 3. Results and discussion

Ink formulation using acrylic-styrene resin yielded a low viscosity (Fig. S1), fast-drying waterborne ink that could be easily applied to any substrate by spin coating and rod coating. Moreover, once dried, the printed ink could not be removed with water since the resin entangles upon drying. The resulting film was also conductive. Spin coated and rod coated films onto Valox™ had a sheet resistance of about 600 Ω □<sup>-1</sup> and 1800 Ω □<sup>-1</sup> respectively. Thin and homogeneous films could be printed using both techniques (Fig. S2). Bending of CNT ink-coated plastic substrate did not affect sheet resistance substantially, proving that the conductive film was mechanically stable (Fig. 1).

The use of an acrylic-styrene resin specially developed for inks and overprinting varnishes confers desirable properties to the CNT inks presented in this work, such as water resistance, fast drying, good

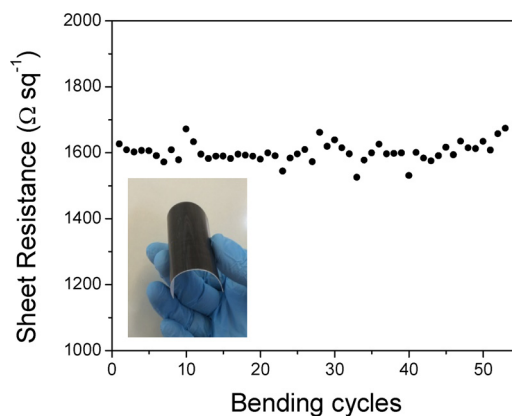


Fig. 1. Sheet resistance of rod coated CNT ink film vs. bending cycles. 53 bending cycles were performed as shown in the inset picture.

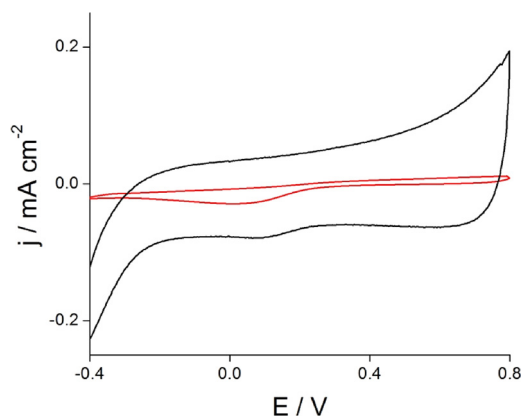


Fig. 2. Cyclic voltammogram obtained at a platinum (red) and a CNT ink coated electrode (black) in 0.1 M phosphate buffer solution of pH 7.4 at a scan rate of 0.05 V s<sup>-1</sup> (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

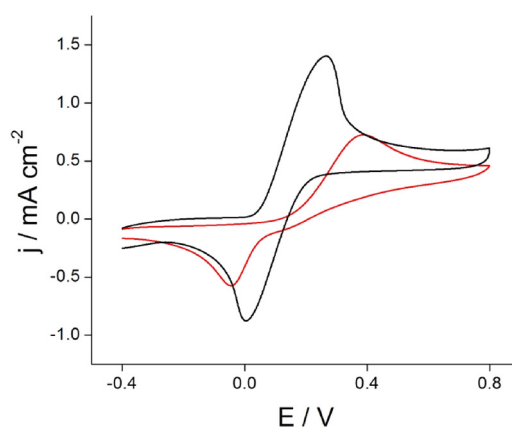
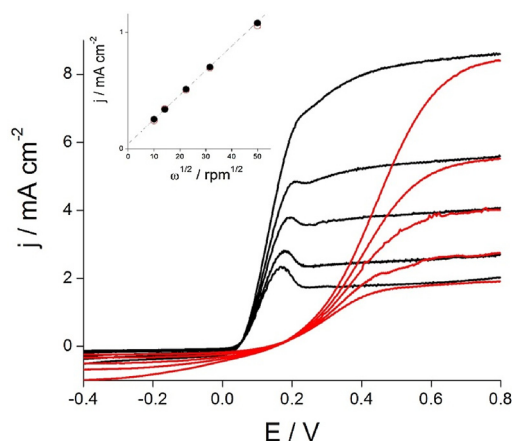


Fig. 3. Cyclic voltammogram obtained at a platinum electrode (red) and a CNT ink coated electrode (black) of 4 mM hydroquinone in a 0.1 M phosphate buffer solution of pH 7.4 at a scan rate of 0.05 V s<sup>-1</sup> (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

adherence to different substrates, and rub resistance. CNT ink could also be deposited homogeneously by rod coating onto untreated Valox™ substrates, suggesting that the rheological and wetting properties of the ink could be adequate for rotogravure or flexographic printing. Rod coating is also suitable for large-area coatings. These features are particularly important for this product regarding potential technological



**Fig. 4.** Linear polarization of rotating disk electrodes obtained at a pristine Pt electrode (red) and a CNT ink coated electrode (black) of 4 mM hydroquinone in 0.1 M phosphate buffer solution of pH 7.4 at different rotation frequencies (from bottom to top: 100, 200, 500, 1000 and 2500 rpm). Inset: Levich plot (experimental points of the limiting current for both electrodes overlap) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

applications such as roll-to-roll production of electrodes for biosensors. Moreover, the addition of PVP helped to stabilize CNT suspension. The stabilizing effect of PVP for CNT suspensions [33] has been combined with the film properties conferred by the acrylic-styrene resin, allowing to obtain a CNT ink that remained stable for several months.

Fig. 2 shows the cyclic voltammograms obtained at a Pt electrode and an ink coated electrode in a 0.1 M phosphate buffer solution of pH 7.4. Both voltammograms displayed a capacitive behavior. It can be noticed that the current for the coated electrode is considerably higher than that for the uncoated electrode. The capacity could be estimated as the ratio between measured current and the scan rate, from which values of around  $70 \mu\text{F cm}^{-2}$  for the Pt electrode and  $1.3 \text{ mF cm}^{-2}$  for the ink coated electrode were obtained. This reflects an increase of about 20 times in the capacitive current observed for the coated electrode. Considering a typical value of  $10 \mu\text{F cm}^{-2}$  for the double layer capacity, an increase of the electroactive surface by more than a hundred times can be estimated for the coated electrode with respect to its geometrical area. This considerable increase in the electroactive surface is in accordance with the topographic and phase images obtained by

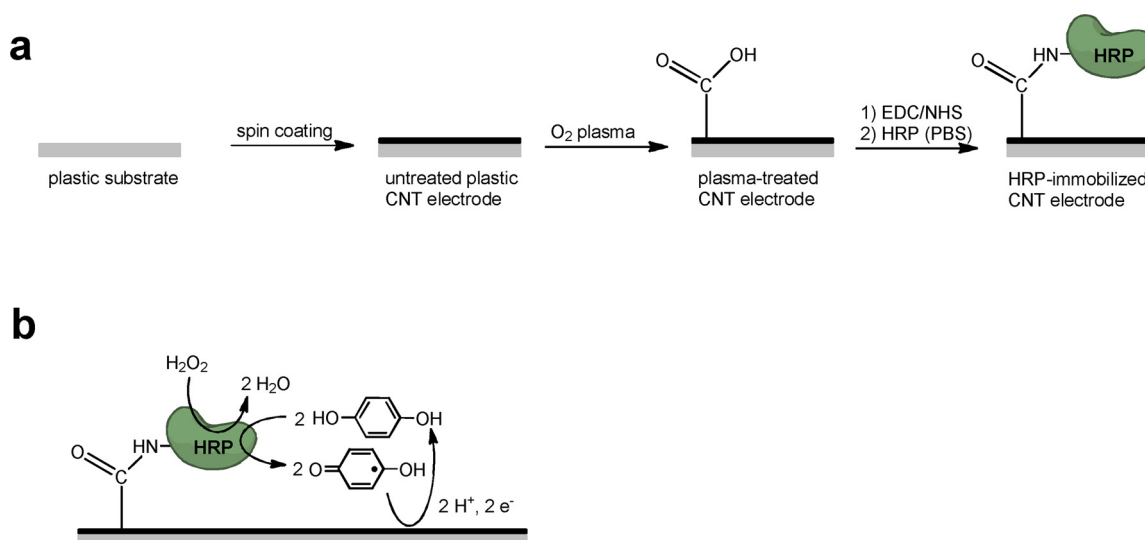
AFM (Figure S3), where CNTs can be seen covering completely the available surface.

The cyclic voltammograms obtained after the addition of 4 mM hydroquinone in a 0.1 M phosphate buffer solution of pH 7.4 are displayed in Fig. 3. The oxidation and reduction waves of hydroquinone can be observed in both voltammograms. However, the peak potential difference is considerably lower for the ink coated electrode (about 0.25 V vs. 0.42 V). The values of the peak current are also higher for the coated electrode, about twice as much for the anodic peak. Both the decrease of the peak potential difference and the increase in the peak current indicate that the CNTs catalyze the oxidation of hydroquinone and the reduction of the oxidized species, benzoquinone [34].

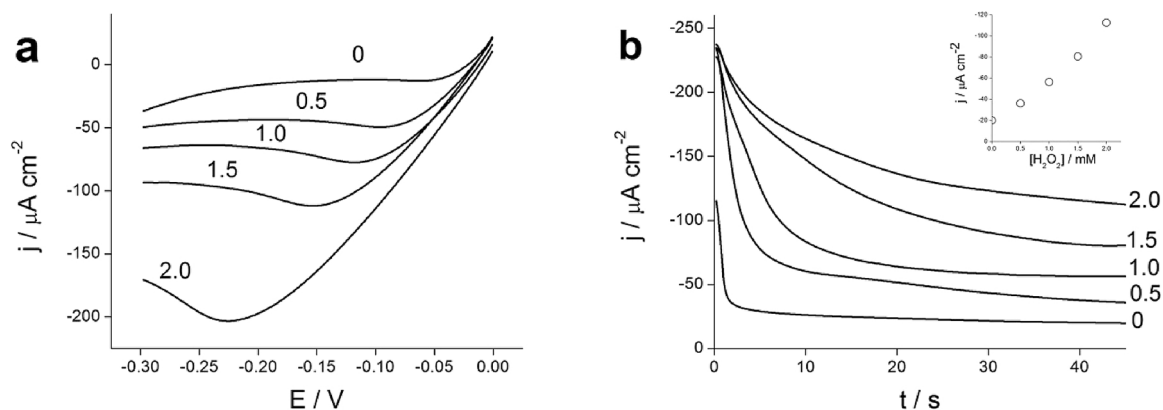
Figs. 3 and 4 show that the electrodes coated with the CNT ink exhibit a catalytic behavior towards the oxido-reduction of hydroquinone/benzoquinone. The catalytic properties of CNT have been reported before. However, it is worth emphasizing that the CNT ink electrodes were used here without further treatment, so a layer of PVP, which was used to stabilize the CNT suspension, was still present surrounding the nanotubes. This PVP layer did not seem to have been an impediment for the redox reaction of hydroquinone. It is apparent that hydroquinone can easily permeate the thin layer of PVP and reach the CNT surface where the electron transfer reactions take place. It is also worth noting that the acrylic-polystyrene resin used to obtain a mechanically robust film did not act as a barrier for the accessibility to the electroactive surface of CNTs.

In order to explore the catalytic behavior of the CNT ink coated electrodes, measurements of linear polarization were carried out at a rotating disk electrode (Fig. 4). It was found that the onset for the anodic current took place at about +0.2 V for the naked Pt electrode, while for the coated electrode, it occurred almost at 0 V. Additionally, the increase in current was much abrupt. The values of limiting current were similar for both electrodes and Levich plots showed a close-to-zero intercept.

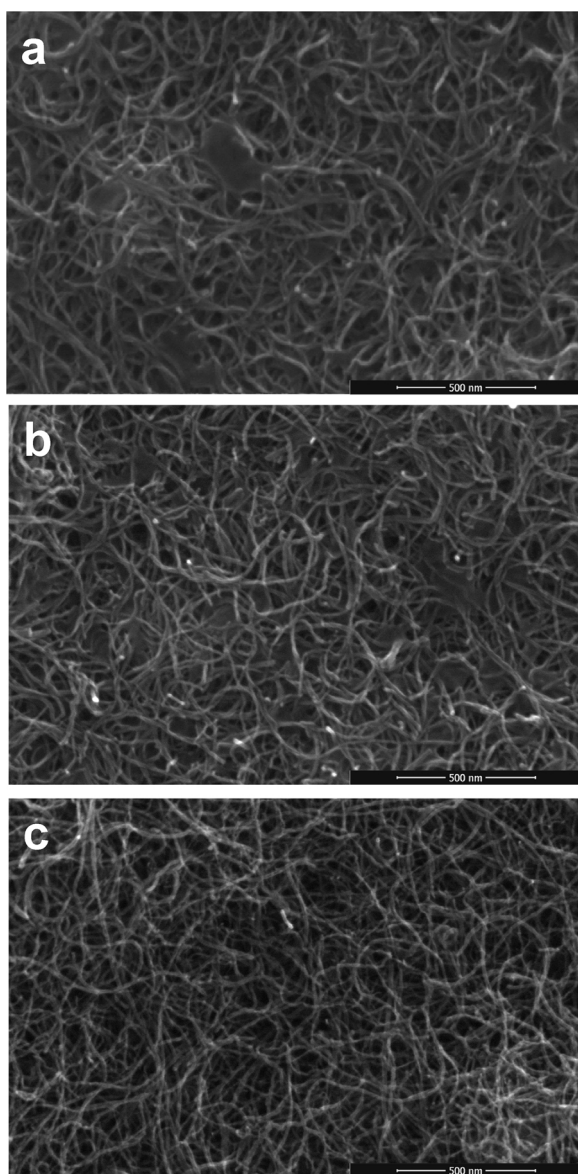
Another distinctive feature of the current-potential curves obtained at the CNT ink coated electrodes is that the current attained a peak before setting at the limiting current. This feature has been described before as characteristic of reversible systems. According to Pleskov [35], in the case of fast electrode reaction controlled by the mass transport of reactants to the electrode surface, the current exhibits a maximum when high scan rates are used. These peaks regard a similarity with the maxima observed in cyclic voltammograms responding to the Randles-Sevcik equation. The peak current density depends on the square root of the ratio between the scan rate and the rotation



**Fig. 5.** (a) Steps for the preparation of HRP-immobilized CNT electrode. (b) Reduction of hydrogen peroxide catalyzed by HRP immobilized onto a CNT ink coated electrode.



**Fig. 6.** Current-potential curves at a scan rate of  $0.02 \text{ V s}^{-1}$  (a) and amperometric response for an applied potential of  $-0.23 \text{ V}$  (b) of  $4 \text{ mM}$  hydroquinone in  $0.1 \text{ M}$  phosphate buffer solution of pH 7.4 at a CNT ink coated electrode with immobilized HRP with different concentrations of  $\text{H}_2\text{O}_2$  (0, 0.5, 1, 0.5 and  $2 \text{ mM}$ ). Inset: Plot of current measured at  $45 \text{ s}$  with an applied potential of  $-0.23 \text{ V}$  vs.  $\text{H}_2\text{O}_2$  concentration.



**Fig. 7.** Scanning electron microscopy of CNT ink electrodes untreated (a) and treated with oxygen plasma during  $20 \text{ s}$  (b) and  $180 \text{ s}$  (c).

frequency (linear polarization curves are shown in Fig. 4).

Enzymatic CNT electrodes were prepared by coating a plastic substrate with the CNT ink followed by the covalent immobilization of HRP as shown in Fig. 5a. These enzymatic electrodes were tested for the detection of hydrogen peroxide, using hydroquinone as a redox mediator. HRP catalyzes the reduction of hydrogen peroxide to water and the oxidation of hydroquinone to semibenzoquinone [36]. Semibenzoquinone is an unstable radical product in aqueous media and may undergo to disproportionation to yield benzoquinone and hydroquinone [37]. Both oxidized species can be reduced electrochemically at the electrode surface at the same applied potential. Therefore, a current proportional to hydrogen peroxide concentration can be measured if the electrode potential is set at a convenient value (Fig. 5b).

As shown in Fig. 6a, cathodic linear polarization curves presented increasing current values with increasing hydrogen peroxide concentration. Fig. 6b shows the current transients obtained at a constant applied potential of  $-0.23 \text{ V}$  for different hydrogen peroxide concentrations, as well as the current-concentration curve resulting at a measurement time of  $45 \text{ s}$  (inset).

The surface of plasma-treated CNT electrodes was examined by scanning electron microscopy and atomic force microscopy (Figs. 7 and S3 respectively). CNTs could be clearly seen in the images of the printed electrodes treated with oxygen plasma for different times (0, 20, and  $180 \text{ s}$ ). In the untreated electrodes, the CNTs and the resin could be seen covering part of the CNTs and the voids between them.

After a plasma treatment of  $20 \text{ s}$ , a partial removal of resin could be noticed without any change in CNT morphology. On the other hand, in the sample treated for  $180 \text{ s}$ , the resin at the surface seemed to have been eliminated and the CNTs presented a diminished diameter, indicating that degradation of the CNT structure has occurred.

Sheet resistance of printed electrodes with different plasma treatment times were measured (Fig. 8). It was found that short treatment times (up to  $20 \text{ s}$ ) produced a decrease in the sheet resistance of the electrode, whereas further treatment produced the opposite effect.

Oxygen plasma treatment exerts an oxidizing effect. SEM images shown in Fig. 7 suggest that organic polymers (PVP, acrylic-styrene resin) were more susceptible to oxygen plasma oxidation and could be removed after a relatively brief oxygen plasma treatment, while degradation of CNT seemed to require longer treatment times. Thus, the decrease of sheet resistance observed for short treatment times could occur probably due to the removal of resin by oxygen plasma, which enhanced physical contact and connectivity among neighboring CNTs. An increase of the sheet resistance for longer treatment times could be explained by the degradation of the conductive network due to oxidation of CNTs. At this point, mechanical stability and functional properties of the CNT electrodes were compromised.

Cyclic voltammetries were also performed using working electrodes



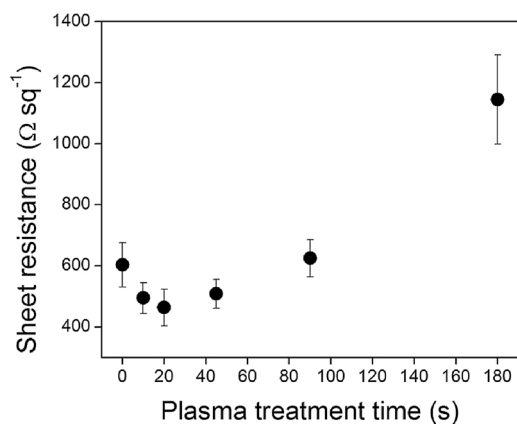


Fig. 8. Sheet resistance of spin coated CNT electrodes after different treatment times with oxygen plasma.

with different treatment times (Fig. 9). It was found that potential peak separation was not greatly affected by plasma treatment times up to 90 s, whereas treatments of 180 s yielded a substantial increase in the peak separation. Moreover, an increase in the  $iR$  drop was observed as the plasma treatment time increased. Peak current remained almost constant up to 45 s of plasma treatment and decreased dramatically for

further plasma treatment. The increase of  $iR$  drop could be attributed to the swelling of the CNT layer. As part of the resin was removed, solvent molecules could access the space between the entangled CNTs, reducing contact between neighboring CNTs at the surface. For plasma treatments longer than 45 s, the exposed CNTs at the surface started to degrade, leading to a decrease of the peak current and an increase of the peak separation when the conductive structure of the electrode became severely damaged. Although it has been reported that oxidation of CNTs can enhance electron transfer kinetics for  $\text{Fe}(\text{CN})_6^{3-/4-}$  [38], the electrocatalytic behavior of CNT ink electrodes was not significantly affected by short plasma treatments. These results suggest that short plasma treatment promoted preferentially the oxidation of the resin with little effect on CNTs. The optimal oxygen plasma treatment time results from a compromise between the need of promoting the generation of carboxylic groups and the degradation of the material. As a conclusion from electrical and electrochemical measurements, 20 s of oxygen plasma was found as the optimal time for enhancing conductivity and generating functional groups for enzyme immobilization while keeping an acceptable electrochemical behavior.

The origin of the electrocatalytic effect of carbon nanomaterials has been discussed before. It has been claimed that the major contribution to these effects are due to the presence of traces of metallic catalysts used for the CNTs growth and defects in the CNT structure [39]. In our case, the CNT ink electrode was a complex matrix where defects were present within the carbon nanotubes, especially after oxygen plasma

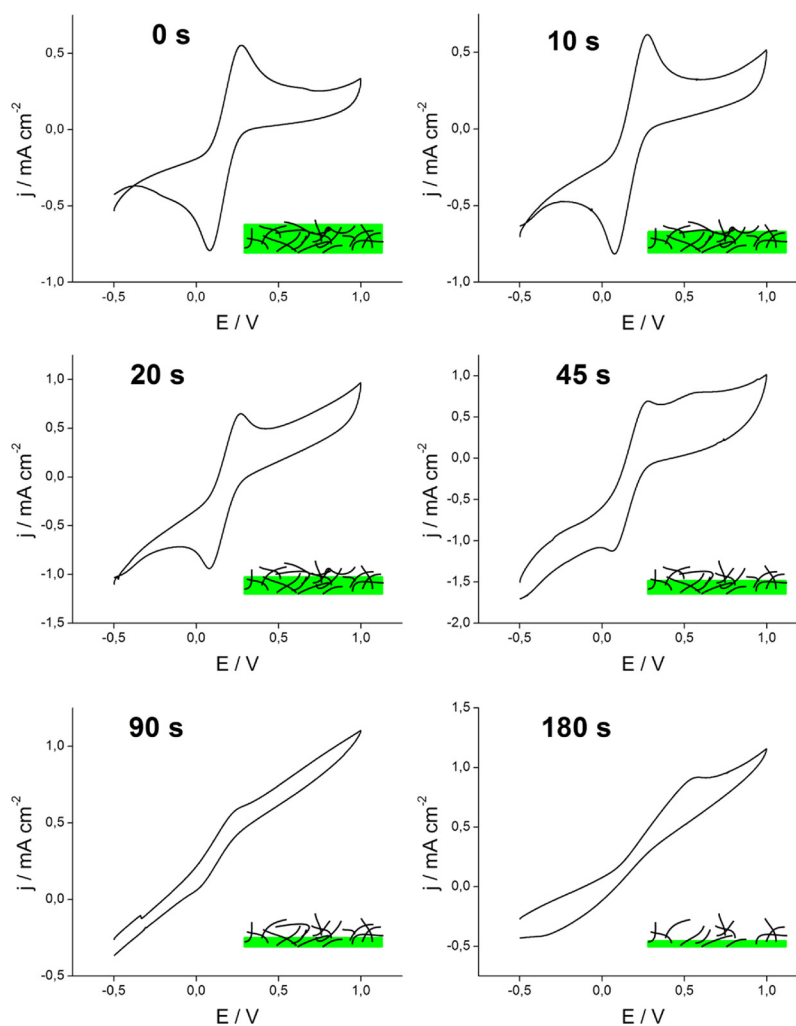


Fig. 9. Effect of plasma treatment time on the cyclic voltammograms of 2.5 mM  $\text{K}_4[\text{Fe}(\text{CN})_6]/\text{K}_3[\text{Fe}(\text{CN})_6]$  redox couple in 0.1 M KCl. Schematic representations of the cross sections of the electrodes with CNTs (black) and acrylic-styrene resin (green) were included next to each voltammogram (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

treatment. The introduction of defects on CNTs can also be achieved by electrochemical cycling [15,19]. As pointed out before, the CNT ink electrodes presented in this work showed electrocatalytic behavior without any treatment and the oxygen plasma treatment used for protein immobilization did not alter significantly their electrochemical properties.

In order to assess the reproducibility of the electrochemical behavior of the CNT electrodes, different ink batches were prepared, used for printing electrodes, and their voltammetric characteristics were analyzed (Fig. S5). The peak potential difference and peak current have not been significantly affected within different batches, showing that the electrocatalytic effect is reproducible.

#### 4. Conclusions

A waterborne CNT ink was used to prepare thin film flexible electrodes. CNT thin films, used without further treatment, presented a high electroactive surface and catalytic properties, e.g. for the electro-oxidation of hydroquinone. Horseradish peroxidase was successfully immobilized onto the surface of the CNT ink electrodes, employing an oxygen plasma treatment followed by covalent linking, using the carbodiimide reaction. The enzymatic electrodes showed a good catalytic behavior towards the reduction of hydrogen peroxide. In summary, the electrodes prepared using the CNT ink described here can be fabricated using fast roll-to-roll process applying a single layer of ink, providing mechanically and chemically robust films, and showing the desired electrochemical characteristics reported for amperometric measurements of CNT electrodes. Moreover, covalent immobilization of a protein onto the electrode for a biosensing electrode fabrication could be achieved while keeping their electrochemical behavior.

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