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Surface activation of CNT Webs towards layer by layer assembly of biosensors

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Several surface activation methods such as chemical, electrochemical and plasma have been used for enhancing the electrochemical performance of carbon based electrodes for various applications. However, some of these surface activation methods may not be useful depending on the chemical and physical properties of the activated surface. Herein we investigate the surface activation of carbon nanotube (CNT) webs by electrochemical and plasma techniques to enhance their electrochemical performance and enable the fabrication of a biosensor using the layer-by-layer (LBL) approach. The pretreated CNT webs were characterized by SEM, TEM, Raman, XPS and electrochemical methods. TEM images and Raman analysis showed an increase in the level of surface defects upon pretreatment with higher number of defects after electrochemical pretreatment. XPS analysis showed an increase in the level of oxygen functional groups after pretreatment (4 to 5 times increase) which resulted in enhanced water wettability especially for plasma pretreated CNT webs. The pretreated CNT web electrodes also showed an enhanced electrochemical activity towards the oxidation and reduction of different redox probes with higher sensitivity for the electrochemically pretreated CNT web electrode that was accompanied by a higher level of noise in amperometric measurements. A highly linear response was obtained for the untreated and the electrochemically pretreated CNT web electrodes towards the amperometric detection of NADH (R^2 of 0.9996 and 0.9986 respectively) while a non-linear response was observed for the plasma pretreated CNT web electrode (R^2 of 0.8538). The pretreated CNT web electrodes enabled the fabrication of a LBL biosensor for alcohol detection with highest operational stability obtained for the plasma pretreated CNT web surface.

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1. Introduction

Carbon based electrode materials can be activated by a number of methods which can lead to improved electrochemical activity apart from the introduction of negatively charged functional groups on their surface. These methods include but are not limited to, chemical, electrochemical and plasma treatment. Chemical methods rely on using strong oxidizing agents and acids with the aid of heat or ultrasonication to oxidize the carbon surface and create negatively charged groups such as hydroxyls and carboxylic acids. Different oxidizing agents such as nitric acid, hydrogen peroxide, ozone, sodium permanganate, sodium hypochlorite or their mixtures amongst other oxidizing agents have been successfully used with different carbon based materials such as carbon fibers,[1] carbon nanotubes[2,3] and graphene.[4] Despite the advantages of this surface activation and functionalisation approach, this method is relatively harsh and can cause degradation of the tested material and loss of electrochemical activity. Electrochemical methods on the other hand offer a gentler and controlled approach for surface pretreatment with better control of treatment parameters such as current, potential and time. Electrochemical pretreatment methods have also been successfully used with different carbon based materials that have shown great improvement in their electrochemical activity.[5–7] Both chemical and electrochemical methods however need to be applied in solution which would add another complexity in recovering and cleaning of the treated materials afterwards. The last technique which is widely used as a cleaning and surface activation method is plasma. Several types of plasma treatments have been used earlier to modify the surface of different materials including carbon and silicon to introduce different functional groups such as amino, carboxylic acid and hydroxyl groups by choosing a related gas or material.[8,9] Air or oxygen plasma has been shown effective in introducing negatively charged functionalities onto the surface of CNTs such as hydroxyl and carboxylic acid groups for different sensor applications.[10–13]

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Despite the novelty of these pretreatment methods in activating carbon surfaces, their effectiveness greatly depends on the structure and surface morphology of the treated material. An earlier study comparing the electrochemical activation of ARC and CVD based CNT showed dramatic enhancement in the electrochemical performance of the ARC-CNT and negligible effect on the CVD ones. This was attributed to the anodic preanodization effectively breaking the basal-plane end caps of ARC-CNT thereby exposing edge plane defects, similar to those already present in the open-end caps of CVD-CNT.[6]

CNT webs are a novel form of CNTs produced by drawing CNTs away from the front face of specially grown 'forests' of aligned CNTs.[14–16] CNTs are drawn as a continuous pure CNTs 'web' of around 20 μm in thickness for a single sheet with high porosity (optical transmission ~80%). The web can adhere to a solid surface and get densified to about 50 nm in thickness by wetting with a solvent and drying. CNT webs mainly comprise of highly pure and well-aligned multi-walled CNTs (MWCNTs), with some occasional cross fibers (mean diameter ~10 nm) and are electrically conductive.[14] Due to their unique structure and high electrochemical activity, they have been shown to be useful in the fabrication of sensors for pesticides detection in water[17] and for solar cell applications.[18,19] However their use in biosensor fabrication has not yet been fully explored and will be investigated in this work. Among the different techniques used for biosensor fabrication, the layer-by-layer (LBL) approach represents a feasible and robust protocol that leads to stable and sensitive biosensors.[20] This approach though relies on the interaction between oppositely charged surfaces being laid down in an alternating manner.[21]

In this paper we investigate different pretreatment methods to activate and functionalize the surface of CNT webs with negatively charged groups towards the development of a biosensor using the LBL approach. The pretreated CNT web electrodes will be characterized by electrochemical, spectroscopic and optical methods to assess the presence of any defects and/or any functional groups on the surface and their effect on the electrochemical activity of the CNT webs. Alcohol dehydrogenase (ADH), will be used in this study as a model enzyme for the construction of the biosensor and will be used for alcohol detection according to the equation below.

$$\text{Ethanol} + \text{NAD}^+ + \text{H}^+ \xrightarrow{\text{ADH}} \text{Acetaldehyde} + \text{NADH}$$

where NAD^+ is used as the enzyme (ADH) cofactor.

2. Experimental

2.1. Chemicals and reagents

Alcohol dehydrogenase from *Saccharomyces cerevisiae* (310 unit per mg solid), NAD^+ and NADH were purchased from Sigma-Aldrich. Alumina ceramic plates were purchased from CoorTek Inc. (Grand Junction, CO 81505, USA). Other reagents were commercially available and were of analytical reagent grade. All solutions were prepared using double-distilled water.

2.2. Electrode preparation

Spinnable CNT forest synthesis is based on an optimized process described in detail elsewhere.[14] The CNT growth was performed in a 3 zone quartz furnace tube (95 mm reactor). The reaction was carried out at atmospheric pressure using flows of C_2H_2, He and H_2 gases. The process is modified with an acetylene and H_2 concentration of only 2.5% ($He/H_2/C_2H_2$ = 4000/100/100 sccm) and running time of 20 minutes. Analysis by TGA, EDX, and TEM of the CNT forest shows very low amorphous carbon content and no trace of the iron catalyst (data not shown).

A prototype CNT web electrode was constructed using drawn CNT webs laid down onto alumina strips (33.8 × 10.0 × 0.635 mm) and solvent densified/bound to the surface with acetone to enable good adhesion with the support. Sets of six matched samples were prepared simultaneously using a winding device with the amount of CNT being controlled by the width of the web, the degree of insulation, and the number of turns applied (Fig. 1A). Typically, about 8.0 mm wide and 20 turns are used. Insulation of the remaining body of the CNT web was made using PVC tape.

2.3. CNT-Web electrode pretreatment

Chemical pretreatment was achieved by incubating the CNT web electrode in a mixture of concentrated sulfuric and nitric acids (3 : 1) and sonicating for 2 h. Electrochemical pretreatment was achieved by inserting the CNT web electrode into phosphate buffer solution (0.05 M phosphate, pH 7.4) with 0.1 M KCl and applying a potential of 1.5 V (*vs.* Ag/AgCl ref.) for 3 minutes with stirring. For plasma treatment, the electrode active surface area was subjected to air plasma under low pressure (270 mTorr) for 1 min using a power of 900 watts. Pretreatments were based on optimized conditions.

2.4. Enzyme immobilization

The untreated or pretreated 20 CNT web layers electrode was placed in 0.1% chitosan (in 1% acetic acid) for 12 h at 8 °C, washed with water and dried for 2 h at room temperature. Then the electrode was incubated in 2.5% glutaraldehyde in phosphate buffer for 1 h, followed by washing with water and drying for 2 h at room temperature. Finally the electrode was incubated in 0.1 mg ml^{-1} ADH in phosphate buffer for 12 h at 8 °C, washed with phosphate buffer then water and dried for 2 h at room temperature. All electrodes were kept in dry conditions just before electrochemical measurement when they were washed and incubated in phosphate buffer.

2.5. Apparatus

Amperometry and cyclic voltammetry (CV) measurements were performed using a computer controlled Autolab PGSTAT302N potentiostat (Ecochemie, NL) with a three-electrode configuration. The 20 CNT web layers electrode was used as the working electrode, the reference electrode (Ag/AgCl electrode, Model RE-5B, MF-2079 Bioanalytical Systems Inc. (BASi), West Lafayette, IN 47906, USA), and the counter electrode (a bright

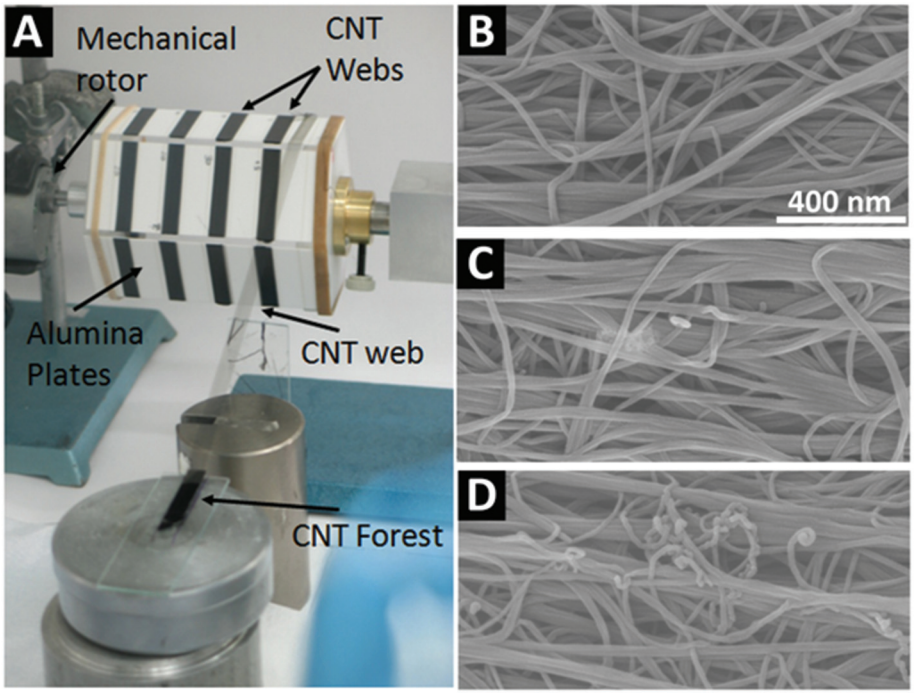

Fig. 1 Photograph of the unit used to prepare the 20 CNT web layers electrodes using alumina plates (A). SEM images of the untreated (B) electrochemically pretreated (C) and plasma pretreated (D) CNT web electrodes.

platinum wire) were inserted into the 50 mL glass cell (Amber glass, homemade) through holes in its Teflon cover.

Air plasma treatment was achieved using Europlasma instrument with an RF-generator of 1000 watts (40 KHz) capacity.

Scanning Electron Microscope (SEM) images were obtained using an FEI Helios unit at an applied electron accelerating voltage of 5 kV (spot 2). Transmission Electron Microscope (TEM) images were obtained using an FEI Tecnai-G20 unit at 200 kV.

Raman spectroscopy analysis was performed using a Renishaw InVia Raman Microscope at a wavelength of 514.5 nm.

X-ray photoelectron spectroscopy (XPS) analysis was performed using an AXIS Ultra DLD spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al Kα source at a power of 180 W (15 kV × 12 mA), a hemispherical analyser operating in the fixed analyser transmission mode and the standard aperture (analysis area: 0.3 mm × 0.7 mm).

2.6. Procedure

A 20 CNT web layers/alumina plate electrode was used either untreated or after pretreatment electrochemically or using air plasma prior to any electrochemical measurements. The apparent surface area of the CNT web electrode (8.0 mm × 5.0 mm) is 40.0 mm^2. The actual electroactive surface area of the untreated CNT web electrode with 20 single CNT web layers was calculated using the measured cyclic voltammetry to be 57.0 mm^2. The plasma and electrochemically pretreated CNT web electrodes had an electroactive surface area of 100.0 mm^2 and 120 mm^2 respectively.

Both amperometric and CV measurements were performed at room temperature under quiescent conditions for CV and under stirring for amperometry. Amperometric measurements were performed after applying the desired working potential and allowing the transient baseline current to decay to a steady-state value.

3. Results and discussion

3.1. CNT web electrode fabrication

Due to their high flexibility, CNT webs enable the design of electrodes with different geometries such as planar, yarn, ring, and ribbon.[14] The simplest configuration is the planar or disc electrode which is shown in Fig. 1A. This configuration is suitable for the mass production of electrodes using the setup shown in Fig. 1A and will be used throughout this study. To maintain better compactness between the 20 CNT web layers and to have good adhesion to the alumina plate surface, the 20 CNT web layers were densified by using few drops of acetone. Upon densification, the thickness of the CNT web layers decreased to one third of the original thickness as was reported earlier.[14] The quantity of CNTs can be controlled by the number of CNT web layers determined by the number of winding device turns (Fig. 1A) or by the electrode electro-active surface area controlled by the insulation process afterwards. It is apparent from Fig. 1A and B that CNT in the webs maintain a high degree of alignment with occasional cross CNT fibers.

The aim of this study was to assess the effect of surface pretreatment methods such as chemical, electrochemical and plasma on the CNT web surface morphology and electrochemical activity besides its ability to introduce some oxygen surface functionality that will enable the design of a biosensor using the LBL approach.

The first pretreatment method involved chemical pretreatment with sonication of the CNT web in a mixture of concentrated sulfuric and nitric acids (3 : 1) for 2 h. This method has previously been used with loose CNTs and shown useful in introducing hydroxyl and carboxylic acid groups and to increase their hydrophilicity and dispersion in water.[2] However, this method was not feasible with the CNT webs since it resulted in complete disintegration and loss of the web structure due to the high acidity and sonication effect. The other two techniques *i.e.* electrochemical and plasma pretreatment were both feasible as no damage to the CNT web structure seemed to occur.

3.2. SEM of the untreated and pretreated CNT web electrodes

In order to assess the effect of the pretreatments on the CNT web structure and morphology compared with the untreated CNT web, SEM characterization was performed as shown in Fig. 1B–D. The SEM images did not reveal major differences between the untreated and pretreated CNT webs with the only exception being the relatively higher degree of welding between the adjacent CNTs upon electrochemical pretreatment (Fig. 1C). The CNTs shown in the SEM images of Fig. 1 are grouped together in the form of larger bundles and each single CNT within the web is made of an average of seven inner walls (multiwall); about 450 μm long and around 10 nm in diameter.

3.3. TEM, Raman and XPS analysis of untreated and pretreated CNT webs

To further elucidate on the differences between the untreated and pretreated CNT webs, TEM analysis was performed to study the pretreatment effects at the single CNT level as shown in Fig. 2. It was clearly evident from these TEM images the presence of major defects in the CNT web structure upon pretreatment (circled in red) (Fig. 2B and C) compared to the untreated CNT web (Fig. 2A) with more of these defects present in the electrochemically pretreated CNT web compared to the plasma pretreated CNT web. A close up of the electrochemically pretreated CNT web image (Fig. 2D) indicates severe damage at certain locations along the CNT fiber with damage in some cases reaching the center of the CNT. Pumera *et al.*[22] has previously shown that electrochemical pretreatment of CNTs can cause major defects in the CNT structure exposing the edge plane of MWCNTs and leading to the formation of amorphous carbon which was responsible for the enhanced electrochemical behavior. On the other hand, earlier studies using plasma pretreatment of CNTs[8,23] did not show major defects in the CNT structure but rather an increase in oxygen functional groups. The difference between the results obtained here and earlier work could be due to the use of milder plasma pretreatment conditions. To further confirm the presence of these defects in the electrochemically and plasma

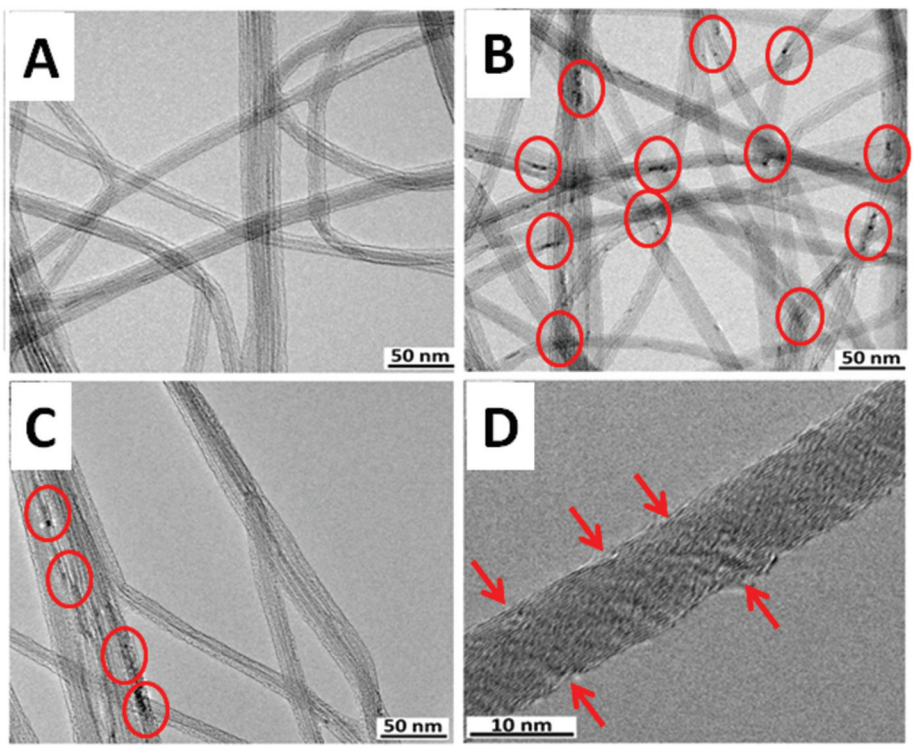

Fig. 2 TEM images of the untreated (A) electrochemically pretreated (B) plasma pretreated (C) and a close up of (B) (D) for the CNT web electrodes.

pretreated CNT webs, Raman analysis was performed and showed an increase in the intensity of the D/G peaks ratio from 0.73 for the untreated CNT web to 0.85 for the pretreated CNT web samples. The increase in the D/G peaks ratio is directly related to the increase in the level of defects in the CNT web structure upon pretreatment. In addition to Raman analysis, XPS analysis showed an increase of oxygen functionality represented by the ratio of oxygen to carbon by a factor of five upon plasma pretreatment and a factor of four upon electrochemical pretreatment of the CNT web surface. This was well in agreement with previous reports on plasma and electrochemical pretreatments of CNTs.[8,22,23] The introduced oxygen functionalities are mostly carboxylic acid and hydroxyl groups according to the Raman and XPS analysis results (data not shown).

3.4. Wettability of the untreated and pretreated CNT webs

To study the effect of these added defects and oxygen functionalities on the surface, the wettability of the untreated and pretreated CNT webs was assessed using water as shown in Fig. 3. As expected, the highly hydrophobic surface of the untreated CNT web showed very poor wettability (Fig. 3A) indicating the absence of any hydrophilic oxygen functional groups. On the other hand, moderate wettability was observed on the electrochemically pretreated surface (Fig. 3B) and complete wettability was observed on the plasma pretreated surface (Fig. 3C). These results were in good agreement with XPS analysis results and earlier reports.[8,22,23] The increased wettability of the plasma pretreated CNT web can be attributed to higher concentration and more homogenous distribution of the oxygen functional groups on the CNT web surface. Despite the increased wettability of the plasma pretreated CNT web surface, the CNT web structure remained intact and stable after washing with water and subsequent electrochemical measurements.

3.5. Cyclic voltammetry of the untreated and pretreated CNT web electrodes

To assess the effect of the different pretreatments on the electrochemical activity of the CNT web electrodes, cyclic voltammetry measurements of the untreated and pretreated CNT web electrodes were performed as shown in Fig. 4 using phosphate buffer (A), ascorbic acid (B), potassium ferricyanide (C) and NADH (D). An increase in capacitance was observed for the plasma and electrochemically pretreated CNT webs (Fig. 4A) due to the increase in electrode electroactive surface area as a result of surface defects and oxygen functional groups. An enhanced electrocatalytic activity was observed with the tested redox probes which resulted in lowering of the oxidation potential by nearly 200 mV for ascorbic acid and NADH. The enhanced oxidation potentials were accompanied by an increase in currents at the two pretreated CNT web electrodes compared to the untreated one. A slightly higher response was observed for the electrochemically pretreated CNT web electrodes compared to the plasma pretreated electrodes while lower overpotentials were observed for the plasma pretreated CNT web electrodes which might be due to the higher level of "edge-plane" defects and electroactive surface area for the electrochemically pretreated CNT web electrodes.

3.6. NADH amperometry at the untreated and pretreated CNT web electrodes

Such enhanced electrocatalytic action by plasma and electrochemical pretreatments facilitates low-potential amperometric measurements of NADH. For example, Fig. 5 compares the amperometric response at +0.30 V (A) and +0.5 V (B) of the untreated (a), plasma pretreated (b) and electrochemically pretreated (c) CNT web electrodes to successive 20 μM additions of NADH. In agreement with the voltammetric data, the untreated CNT web electrode is not responsive at +0.3 V to these concentration changes using this low-detection potential. In contrast, the pretreated CNT web electrodes respond very rapidly to these changes in the NADH concentration, producing steady-state signals within 3–5 s. As expected from the voltammetric data, the electrochemically pretreated electrode showed higher sensitivity compared to the plasma pretreated electrode. The higher sensitivity though is accompanied by a higher noise level probably arising from the higher level of defects. On increasing the detection potential to +0.5 V, all electrodes were responsive to NADH concentration changes with high linearity obtained for the untreated and electrochemically pretreated electrodes (R^2 of 0.9996 and 0.9986 respectively) and poor linearity obtained for the plasma pretreated electrode (R^2 of 0.8538). This nonlinear response could be resulting from the excess negative charge on the plasma pretreated CNT web surface and possible surface passivation of the plasma pretreated electrode at higher potentials which might explain the difference in NADH oxidation currents obtained by voltammetric (Fig. 4D) and amperometric (Fig. 5B) measurements.

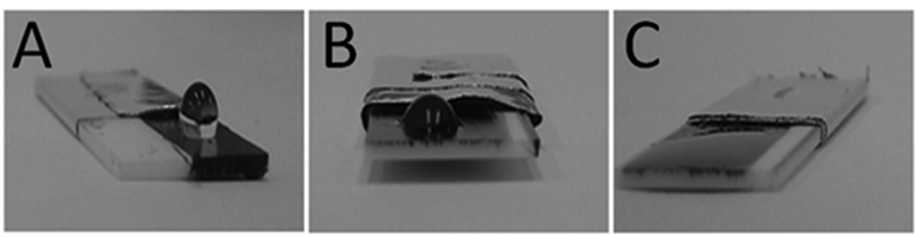

Fig. 3 Wettability of the untreated (A) electrochemically pretreated (B) and plasma pretreated (C) CNT web electrodes using 10 μl water.

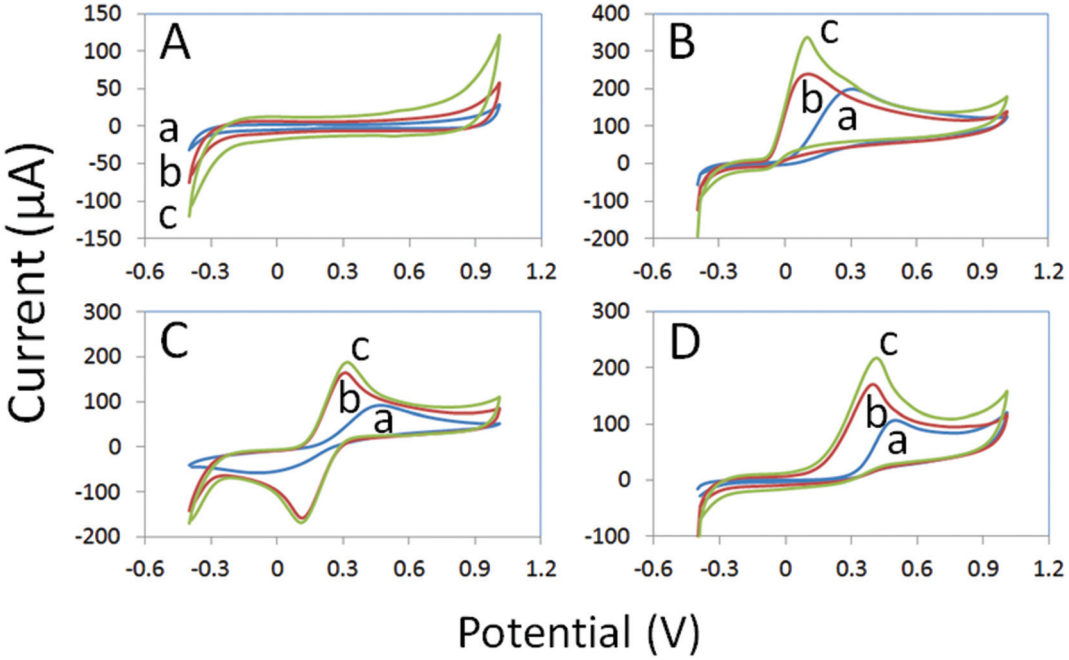

Fig. 4 Cyclic voltammograms obtained at the untreated (a) plasma pretreated (b) and electrochemically pretreated (c) CNT web electrodes in the presence of (A) phosphate buffer solution, (B) 1 mM ascorbic acid, (C) 1 mM $K_3Fe(CN)_6$ and (D) 1 mM NADH. Conditions: phosphate buffer (pH 7.4, 0.05 M) with 0.1 M KCl; scan rate, 100 mV s^{-1}.

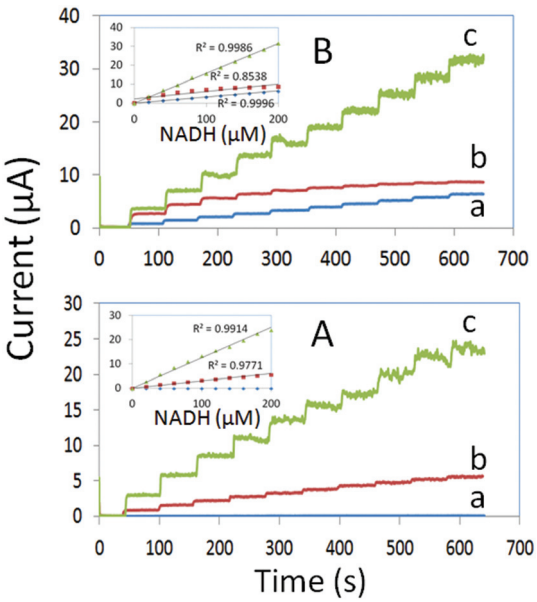

Fig. 5 Current–time recordings obtained on increasing the NADH concentration in 20 μM steps at +0.3 V (A) and +0.5 V (B) using untreated (a) plasma pretreated (b) and electrochemically pretreated (c) CNT web electrodes. The insets of (A) and (B) are the corresponding calibration plots. Other conditions as in Fig. 4.

3.7. LBL assembly and stability of biosensors using the untreated and pretreated CNT webs

The enhanced electrochemical activity of the pretreated CNT web electrodes towards NADH detection would facilitate the design of a dehydrogenase based biosensor for alcohol detection. Taking advantage of the introduced negatively charged oxygen functional groups upon electrochemical or plasma pretreatment, a LBL biosensor design was assessed (Fig. 6A). In this arrangement chitosan was used due to the presence of amino groups which are positively charged in acidic solution and hence would have strong interaction with the negatively charged CNT web surface. This was followed by adding a layer of glutaraldehyde to crosslink the enzyme for additional stabilisation. Finally a layer of the ADH enzyme was added which is negatively charged at pHs >5.5, "the isoelectric point of the enzyme". In agreement with NADH amperomteric measurements (Fig. 5), all LBL biosensors were responsive at +0.5 V (Fig. 6(B)) to incremental 1 mM additions of ethanol in presence of 1 mM NAD^+ as a cofactor with highest sensitivity obtained for the electrochemically pretreated electrode (c) followed by plasma pretreated electrode (b) and the lowest response observed for the untreated electrode (a). The response was quite rapid (2 s) and nonlinear indicating that the enzyme was directly exposed to the solution at the outermost layer of the LBL assembly. By increasing the potential to +0.7 V (Fig. 6(C)), an increase in response was observed for the plasma pretreated electrode (b) while no change in response was observed for the electrochemically pretreated (c) and untreated (a) CNT web electrodes. Evaluation of short-term stability of these LBL biosensors was performed by incubating the different electrodes in phosphate buffer solution for five hours after the initial testing as shown in Fig. 6D. The untreated electrode (Fig. 6D a) suffered a 100% loss in response compared to the initial response (Fig. 6B a). While

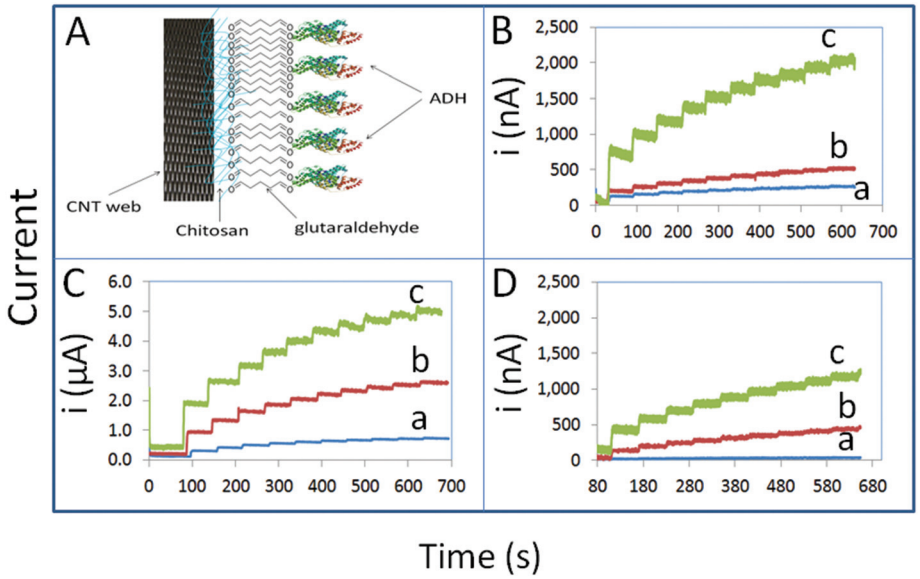

Fig. 6 Schematic of the LBL biosensor assembly (A), current–time recordings of the LBL biosensors using untreated (a) plasma pretreated (b) and electrochemically pretreated (c) CNT web electrodes at +0.5 V (B), +0.7 V (C) and +0.5 V after 5 h incubation in buffer (D). Other conditions as in Fig. 5.

the response at the electrochemically pretreated electrode decreased by 50% (Fig. 6D c) as compared to the initial response (Fig. 6B c). The most stable response was observed for the plasma pretreated electrode where no change in response occurred after this short period of incubation in phosphate buffer solution (Fig. 6D b and B b). Longer term stability assessment showed complete loss of response at the electrochemically pretreated CNT web electrode after 3 days while 80% of the response was still maintained after 20 days of storage at 8 °C in phosphate buffer using the plasma pretreated CNT web biosensor. This stable response for the plasma pretreated electrode reflects better interaction between the different layers of the LBL assembly with each other and with the CNT web surface. All pretreated and untreated CNT web electrodes showed good reproducibility of <5% after 5 repetitive measurements.

4. Conclusions

The experiments and results described above indicate that CNT webs can be activated by techniques such as electrochemical and oxygen plasma treatments which lead to enhanced electrochemical activity without affecting their overall structure and stability. Chemical activation using concentrated acids was not possible due to the instability of CNT webs upon exposure to such harsh treatment. The electrochemically and plasma activated CNT webs showed increased level of surface defects and oxygen functional groups which resulted in the enhanced surface wettability. Based on surface characterisation and wettability results, the defects formed by the electrochemical pretreatment seem to be severe and localized at certain positions on the surface of each single CNT fiber and affecting the different layers of the CNT webs. This pretreatment resulted in the introduction of localized oxygen functional groups as well. Plasma pretreatment on the other hand involved a gentler surface activation that affected mainly the outermost layer of the CNT webs and showed higher and more homogenous distribution of the oxygen functional groups and therefore less defects on the surface compared to CNT webs prepared using the electrochemical pretreatment method. Due to these pretreatments, a LBL alcohol biosensor was successfully fabricated and showed the highest stability with the plasma pretreated CNT webs. More work is still needed to determine the exact nature of the oxygen functional groups resulting from each pretreatment and the stability of these groups upon exposure to air and aqueous medium. Long-term stability assessment of these biosensors will also be important for their practical operation.

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