Multiwalled Carbon Nanotubes as platforms for the design of Biosensors

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ABSTRACT

Carbon Nanotubes (CNT) have attracted a huge interest in the research community due to their unique properties: good electrical conductivity, excellent mechanical properties and chemical stability. An interesting phenomena is the fact that CNT change their electrical properties depending on the absorbates on the surface. This is being exploited for the use of CNT as sensor platforms. In this work, the growth and chemical functionalisation of aligned CNT arrays for the development of electrochemical sensors is presented. The CNT growth process and surface has been tailored to maximise the interaction of the CNTs with the electrolyte. The possible use of the active bio-nano-sensors for mobile monitoring will be discussed in the context of a remote wireless sensors suitable to be integrated for long term patient monitoring, as well as long-haul driver/pilot situations.

Keywords: carbon nanotubes, biosensor, biopotential

1 Introduction

Since their discovery carbon nanotubes (CNTs) have attracted great interest as sensing platforms. They are excellent platforms for developing sensors due the high "effective" area that these nanostructures can occupy, together with their excellent electrical, mechanical and thermal properties and chemical stability [1]. There is a wide range of applications where CNT have been used as sensing platforms, i.e. chemical sensors based on the changes of electrical conductance produced by the adsorption of chemical species [2]; gas ionisation sensors [3] or biosensors where the nanotubes have been chemically functionalised with enzymes that act as transductors [4].

The chemical stability of CNTs makes them also ideal for the design of electrochemical sensors where the inertness of the substrate is specially necessary. Several reports have presented the use of CNTs, in particular multiwalled CNTs (MWCNTs), as electrochemical electrodes. These results have shown that the signal to noise ratio is significantly enhanced due the high specific surface associated to CNTs. This increase in the specific area enhances the contact with the electrolyte and therefore the impedance of the electrode is diminished.

On the other hand, the use of CNTs for the development of human biopotential electrodes has not been explored yet. These signals are of the order of magnitude of a few mV for electrocardiograms and some μV for electromyographs. The use of sensors is usually associated with the necessity of gels to increase the contact area with the human body as well as the enhancement of the ionic exchange with body fluids.

In this work, the use of MWCNTs arrays grown by plasma enhanced chemical vapour deposition (PECVD) for the development of electrochemical sensors will be explored. The work includes the functionalisation of the surface with metal particles that will increase the surface area, therefore, increasing the signal to noise ratio, as well as enhancement of the ionic exchange with the electrolyte.

2 Experimental

The CVD technique is the most suitable method to be scaled up to grow large quantities of CNTs in ordered arrays with CNTs grown at precise locations. In this method, the overall energy expended to the system to grow CNTs is lower than in the case of laser ablation or arc discharge. For this reason, the reaction needs to be catalysed by metallic particles (usually Fe, Ni or Co) which decompose the carbon source gas at their surface. The catalyst was deposited as a film on the surface of highly doped silicon subsrates using thermal evaporation or DC sputtering.

The CVD grown CNTs were synthesized using a DC driven PECVD system with C_2H_2 as the hydrocarbon source and N_2 for dilution purposes. Figure 1 shows an image of the growth system when the plasma is activated. The substrate is heated using a heater plate capable of reaching a temperature of 700 ℃. The anode used in this system is a stainless steel plate with a separation gap of 1.5 cm between the electrodes. The applied bias between anode and cathode was 450 V. The flow rate of the C_2H_2 and N_2 was fixed at 5 sccm and 100 sccm respectively while the chamber pressure was kept constant 3.6 Torr during the 10 minute deposition process.

Scanning electron microscopy using a Hitachi S4000 field emission gun SEM was employed to examine the

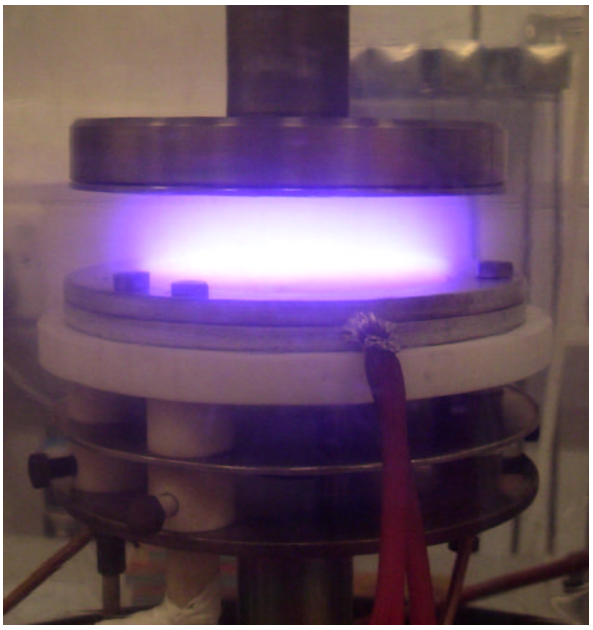

Figure 1: Image of the DC PECVD growth system when the plasma has been ignited.

surface structure of the films. The MWCNTs were also characterised using a Philips CM200 transmission electron microscope (TEM) equipped with energy dispersive X-ray analysis (EDX).

The investigations carried out also include a study of the coating of the CNTs with AgCl. The coating technique used for this study is laser ablation. In this technique, a target is vapourised using a high energy laser pulse. A target made of melted silver chloride was ablated with laser (6 J/cm^2) operated at a wavelength of 248 nm.

3 Results and Discussion

The DC PECVD system produces ordered arrays of MWCNTs as these are aligned during the growth process by the electric field. Figure 2 shows a typical SEM image of an aligned array of MWCNTs . More details of the growth process or the catalyst preparation can be found elsewhere [5], [6]. The distribution and diameter of the CNTs is determined by the distribution of the catalyst particles used during the CVD growth process. This is because the CNTs grow from the Ni catalyst particles deposited onto the surface of the substrate. Figure 2 shows a darker sport at the tip of the CNTs. This dark spot corresponds to thecatalyst particles which in our case is nickel. This is the effect of the tip growth model in which the Ni particle is pushed vertically by the growth front were the carbon precipitates to form the CNT bellow the catalyst.

Figure 3 shows a high resolution TEM image of a

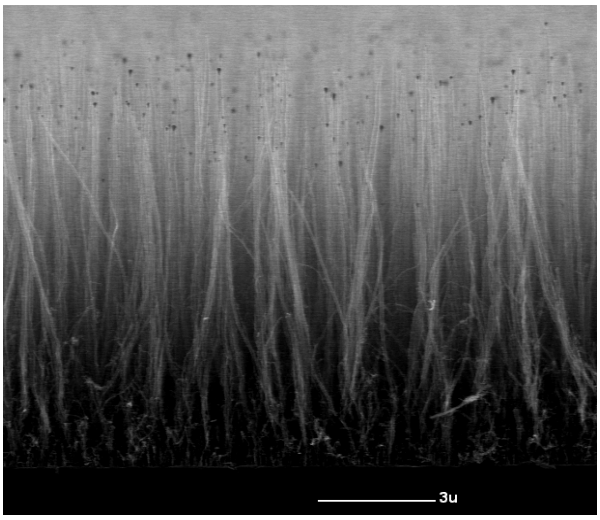

Figure 2: SEM image of an array of MWCNTs grown by DC PECVD. The nickel catalyst particles can be identified at the tip of the CNTs

MWCNT grown using CVD. The Ni catalyst at the top of the tube can be clearly identified, which further confirms the SEM observations that the growth mechanism is a tip growth process [7]. The image also shows the graphitic tube walls as well as the typical defects of CVD grown CNTs.

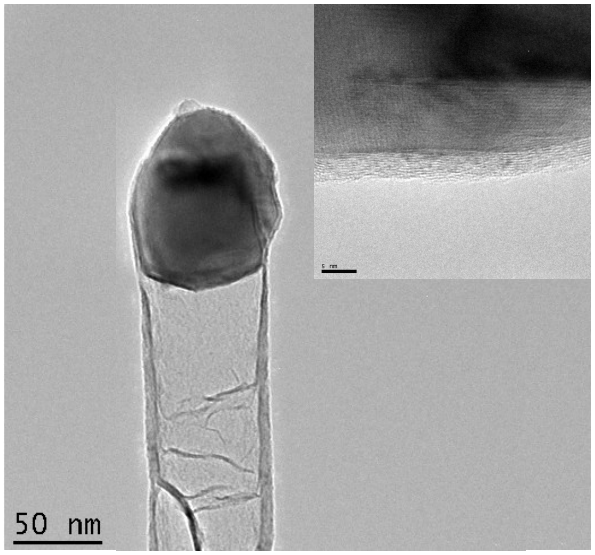

Figure 3: TEM image of a multiwalled MWCNT. The parallel graphene layers can be observed as well as the typical bamboo-like structure associated with the MWCNTs produced by CVD.

For the application of this type of MWCNT arrays for biopotential electrodes an ionic exchange function-

alised layer is desired as a route to increase the signal to noise ratio. The ionic exchange layer consists on a substance that transduces from ionic flows within the body fluids to the electronic voltages to be electronically treated [8]. In our case, the functionalisation has been performed depositing AgCl onto the walls of the CNTs that form the electrodes using laser ablation. Different numbers of laser shots were used to see how it influences the deposited size of silver crystals as well as the coverage of the nanotube surface. The ablated AgCl vapourized and decomposed into metallic silver and gaseous chlorine and the vapours of metal were deposited on the outside wall of the CNTs used as a template. Figure 4(a) shows a SEM image of a CNT array which has been partially covered with Ag. Figure 4(b) presents a magnification of the tubes that shows the Ag particles coating the walls extremely uniformly on the CNTs. Another advantage of such a coating is the fact that the coating also increases the surface area of the electrode which will help to increase the signal to noise ratio.

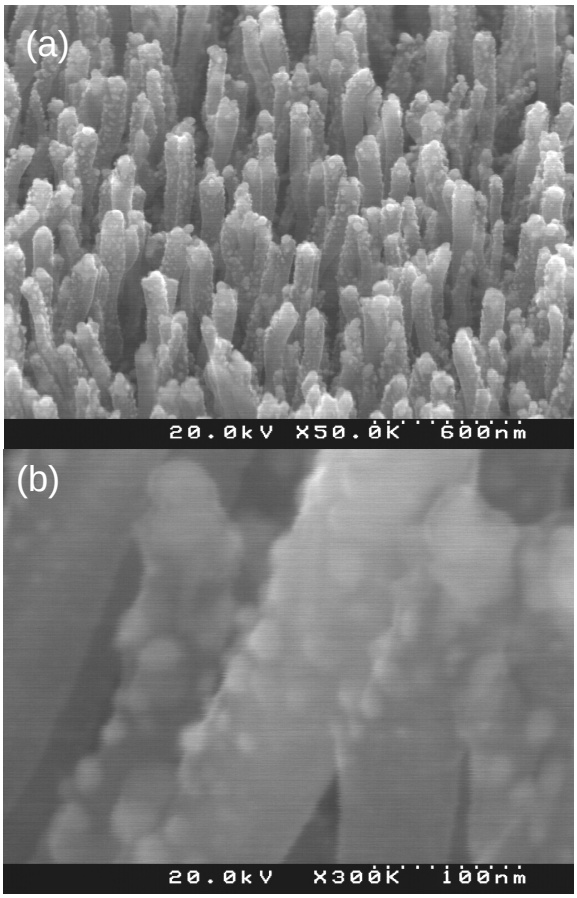

Figure 4: (a) SEM image showing an array of CNTs coated with Ag. (b) Magnification of (a) showing the small Ag droplets covering the walls of the tubes.

Presently, the electrochemical characterisation of such arrays is being performed using cyclic voltammetry. This technique allows to measure the impendance of an electrode in contact with an electrolyte. Also, the development of a fully wireless electronic platform is underway. The platform envisaged is using a self configuring, remote powered, ad-hoc type network which has the ability to dynamically alter the topology of the network to minimize the energy consumption. Ultimately the sensor should be addressable using current networking standards to minimize the complexity associated with connecting the sensors to various monitoring equipment. Thus the solution should be standards based, following closely the Open System Interconnect model. The IEEE 802.15.4 standard addressed this problem by creating a standard for the physical (PHY) and Data Link layer (MAC). This protocol has been created for low data rate and very low power consumption applications. The physical layer works in the 2.4GHz unlicensed, international frequency band. It also supports critical latency devices, thus making it a reliable choice for medical sensing applications.

Using the above stated standards as a platform, a protocol can be designed for the top layers of the 802.15.4 standard which supports 1) multi-hop transmission of data (to minimize power consumption), 2) low power states, 3)available power aware transmission power throttling, 4) ad-hoc, and, 5) self configuring networks. A similar protocol is the Zigbee standard (belonging to the Zigbee Alliance), which implements a few of these functions. This would allow for the application of the sensors by an individual who does not know the internal workings of this Body Area Network, furthermore it leads to faster application times since the sensors will form the most efficient topology to transmit data to the monitoring base.

The monitoring base would be wirelessly powering the nanotube base sensor. A thin film flexible rechargeable battery will constantly be trickle charged by the interrogator (receiver). Possibilities of R.F. power scavenging will also be researched, allowing the sensor to be interrogated while evading the need for a high power R.F powering signal.

4 Conclusions

The growth and functionalisation of MWCNT arrays for the development of electrodes for the measure of biopotentials has been presented. The MWCNT distribution and diameter can be controlled using the CVD process by controlling the catalyst particles deposited onto the substrate. Futhermore, the functionalisation of the surface to improve the ionic exchange properties with body fluids has been presented. For this purpose, the MWCNTs have been partially covered with Ag using laser ablation from an AgCl target. The MWCNTs

are covered with an homogeneous distribution of nanometric sized Ag particles. This strategy has the further advantage of increasing the surface area of the electrode which is usually associated with a smaller impedance. Further investigations will involve the reaction of Ag particles with Cl to create the necessary AgCl. After this process, the electrochemical properties of the resulting arrays will be tested using cyclic voltammetry. Finally, the wireless platform for the development of bio-nano-sensors for mobile monitoring has been discussed.

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