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Short communication

Effect of the surface organization with carbon nanotubes on the electrochemical detection of bisphenol A

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ABSTRACT

This communication reports a comparison study between sensors based on vertically aligned and dispersed single-walled carbon nanotubes on the electrochemical determination of an endocrine disruptor. The vertical alignment of carbon nanotubes enabled an electrocatalytic effect and enhanced the sensitivity of bisphenol A oxidation compared with an electrode modified with dispersed carbon nanotubes. The vertically aligned surface had a remarkable influence on the limit-of-detection obtained for bisphenol A.

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1. Introduction

Carbon nanotubes (CNTs) are attractive for a variety of potential applications due to their unique electrical, magnetic, mechanical, and thermal properties. The ability to manipulate them on a micro to nanometer scale, and the control of the interaction with the orientation on substrate, are extremely important to both. The characterization and application of carbon nanotubes in advanced devices, including nanotube electron emitters, single-molecular transistors, sensors, sensor chips, and chemosensors [1–3].

Different methods for achieving directional growth of the tubes, such as: alignment by electric [4,5] and magnetic fields [6], alignment by mechanical forces [7], self-assembly [8–11] are being developed. Recently, controlled self-assembly of CNTs has been achieved by arranging them with biological molecules. Prominent among these strategies are alignments formed by DNA molecule wrapped CNTs. The DNA molecule is stabilized on the CNT by van der Waals forces, driven by the optimal overlap of the π orbitals of the DNA bases and the carbon hexagons on the cylindrical nanotube, as well as by electrostatic interactions with the phosphate backbone [12–14].

Several studies have reported the formation of films of single-stranded DNA (ssDNA) wrapped CNTs on solid supports for electrochemical applications [15,16]. Methods for the vertical attachment of sulfide modified ssDNA wrapped CNTs on a gold substrate by a self-assembly technique have also been reported [17,18]. However, the importance of alignment for using CNTs as electrochemical sensors has not been considered.

Considering this current state of the art, this study focuses the effect of alignment of single-walled carbon nanotubes (SWCNTs) upon increasing the sensitivity in an electrochemical determination of bisphenol A (BPA).

2. Experimental

2.1. Materials and methods

Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) were performed using a model PGSTAT 30 Autolab electrochemical system (Eco Chemie, The Netherlands). The cell was assembled with a conventional three-electrode electrochemical system: a bare gold (Au) electrode modified with ssDNA/SWCNT or SWCNT as working electrode, a Ag/AgCl/KCl reference electrode and a Pt plate as auxiliary electrode. All electrochemical experiments were performed in 0.1 mol L^{-1} phosphate buffer solution (PBS) pH 6.0 containing 0.1 mmol L^{-1} BPA. CV was carried out at a scan rate of 50 mV s^{-1}. DPV measurements were obtained using a pulse amplitude of 100 mV and step potential of 2 mV. EIS data were obtained using FRA2 software (Eco Chemie, The Netherlands) in a frequency range from 100 kHz to 10 mHz and an amplitude of 10 mV, with 10 data points per frequency decade. Measurements were carried out under open circuit potential (OCP) conditions in 0.1 mol L^{-1} PBS pH 6.0 containing 0.1 mmol L^{-1} BPA.

The morphological characteristics of the electrodes were examined by atomic force microscopy (AFM) using a model Nanosurf

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EasyScan 2 AFM System (Nanosurf AG, Switzerland). The measurements were carried out with non-contact/tapping mode, long cantilever.

2.2. Sensors preparation

The SWCNTs immobilization was carried out as follows. Prior to the modification of the Au surface, 100 mg SWCNTs (98% purity, NanoLab, Waltham, MA, USA) synthesized by thermal chemical vapor deposition were mixed with 100 mL of 5.0 mol L^{-1} of nitric acid (HNO_3) for 5 h, in order to promote the CNTs functionalization [19]. The SWCNTs were then filtered through a Millipore Nylon® filter membrane. The resulting nanotubes were continuously washed using distilled water until the pH of the filtrate was neutral. In the sequence, SWCNTs were dried overnight in a vacuum oven at 120 °C. The formation of the ssDNA/SWCNT hybrid on Au surface was based on the work of Zheng et al. [14]. A thiol-terminated ssDNA (5′-HS-TGG-GGT-TTA-TGG-AAA-TTGGAA-3′) was purchased from Sinapse Biotecnologia (Brazil). First, ssDNA wraps the CNTs by π–π interactions, which involve aromatic rings of the ssDNA molecule nucleotide bases and the hydrophobic side of CNTs; the hydrophilic (sugar–phosphate) of ssDNA is left exposed to interactions with the medium. The formed ssDNA/SWCNTs hybrid is then assembled on the Au surface by spontaneous adsorption of thiol groups. For this, 1.0 mg functionalized SWCNTs was mixed with 500 mL of 1.0 μmol L^{-1} ssDNA solution. The latter was prepared in 0.1 mol L^{-1} PBS containing 10% sodium chloride (v/v). Next, the mixture was sonicated using an ultrasonic horn probe and then centrifuged at 7000 rpm; each process took 45 min. Finally, a previously cleaned bare Au electrode was immersed in the supernatant solution and self-assembled monolayers (SAMs) consisting of ssDNA/SWCNT were formed during 24 h in a refrigerated room at 4 °C.

The dispersed film of SWCNTs on the Au surface was prepared by mixing 1.0 mg of SWCNTs (previously functionalized in 5.0 mol L^{-1} of HNO_3 for 5 h) and 1.0 mL of PBS. The suspension was placed in an ultrasonic horn probe for 30 minutes. Then 10 μL of the dispersion was dropped over the top of the Au electrode surface. The film formed was dried over room temperature.

3. Results and discussion

3.1. Morphological characterization of the sensors

The morphological characteristics of the electrodes were examined by AFM. Fig. 1A displays a typical image of the gold surface, which was shown to be flat and smooth. Based on Au surface topography analyses, the root mean square (RMS) roughness was 3.52 nm. Fig. 1B shows the Au surface after the SWCNT vertical alignment procedure (Au/ssDNA/SWCNT). Under the microscope, it was observed that the SWCNTs were aligned vertically and bundled. The RMS roughness was 66.3 nm whereas the SWCNTs average height was 156.2 nm, with a relative standard deviation of 9.7%. The AFM of the SWCNT assembled over the Au surface via a dispersive method is presented in Fig. 1C. Under microscopy it can be observed that the CNTs were in agglomerates (set by arrows).

This carbon nanotubes clustering is due to the hydrophobic characteristic of the SWCNTs, leading to a low dispersive capacity. However, the image demonstrated that there was no control in the deposition method. Also, the carbon nanotubes clusters increased the RMS almost 2-fold. Based on Au/$SWCNT_{dispersed}$ topography analyses, the roughness was calculated at 136.4 nm.

In order to confirm the presence of vertically aligned CNTs, a study of the monolayer (ssDNA/SWCNT) desorption was performed. The monolayer desorption process is based on the cleavage of the bond Au–S (where sulphur atom is derived ssDNA molecule) according to the study reported by Kawaguchi et al. [20]. Thus, a DPV experiments were carried out using the bare Au, Au/$SWCNT_{dispersed}$ and Au/ssDNA/SWCNT electrodes, with pulse amplitude at 100 mV and step potential at 1 mV, in 0.1 mol L^{-1} of sodium hydroxide (NaOH) as shown in Fig. 1D.

For the bare Au and Au/$SWCNT_{dispersed}$ electrodes was not observed reduction process in the potential region studied. This indicated that no sulphur species was adsorbed on the Au surface.

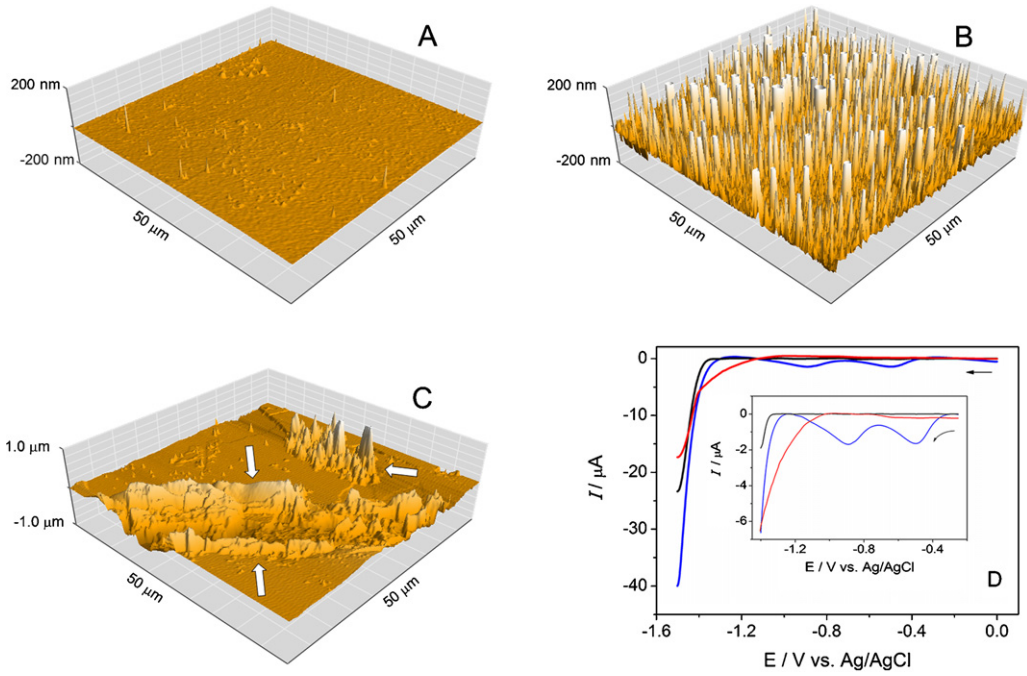

Fig. 1. AFM images of the electrodes: (A) bare Au, (B) Au/ssDNA/SWCNT and (C) Au/$SWCNT_{dispersed}$. (D) DPV voltammograms in 0.1 mol L^{-1} of NaOH for the electrodes: bare Au (black line), Au/$SWCNT_{dispersed}$ (red line) and Au/ssDNA/SWCNT (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

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