



Electrochemical properties of spaghetti and forest like carbon nanotubes grown on glass substrates

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ABSTRACT

Carbon nanotubes (CNTs) have been widely used in many fields of chemical analysis to achieve more sensitive detection systems. In this work, we performed fundamental studies on grown or bottom-up fabricated MWCNTs (both non-oriented and oriented configurations), showing how variables like orientation, density, underlayer deposition, or synthesis time strongly determine their behavior (physical, electrochemical and analytical) as transducers. The electrochemical performance of these surfaces was demonstrated by cyclic voltammetry and chronoamperometry of dopamine (DA) solutions in 0.1 M H₂SO₄. The carbon nanotubes surfaces pre-treated with 1 M HNO₃ lead to increased signals, sensitivity and enhanced limits of detection (LOD). The grown working electrodes (WE) were reproducible and stable over the time. The peak variations gave RSD values of 8%, 4% and 3% for high-density spaghetti-like and ITO or Al underlayered forest-like MWCNTs grown for 30 min, respectively. This study highlighted the importance of controlling the synthesis variables to achieve better analytical parameters.

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1. Introduction

Nowadays there is a strong demand in many fields of chemical analysis to produce highly selective and sensitive detection systems [1]. As a consequence of their large surface-to-volume ratios, nano-structured materials have been widely used to favor electron transfer processes, resulting in improved sensitivities [2]. Special attention deserves carbon-based materials and particularly carbon nanotubes (CNTs) [3]. They have been the focus of intensive research due to their unique properties [4] and particularly their strong electrocatalytic activity, which makes carbon nanotubes extremely attractive for developing highly sensitive electrode surfaces [5–7].

Carbon nanotubes have often been integrated onto electrode surfaces as modifiers [8–11], frequently by random dispersions obtained by mixing them with solvents in the absence or in the presence of dispersing agents [12–15]. However, it is difficult to obtain a homogeneous dispersion (especially in water) [12] and the chemical treatment required to obtain it can degrade them. To use carbon nanotubes as electrode material is essential to preserve

and take advantage of their properties [16]. With this aim, several efforts have been focused on increasing the control over nanotubes distribution, not only by modification of the electrode surface [17,18] but also by direct growth from the substrate [19–21]. This latter strategy is particularly attractive because it can overcome problems related with the dispersion process and provide a good surface attachment. The grown carbon nanotubes can be classified into two main groups: non-oriented (spaghetti-like or disordered) and oriented (forest-like or vertically aligned carbon nanotubes, VACNTs) [22] and they have been grown not only onto metallic [19,23,24] and carbon [5,25,26] materials, but also on surfaces electrically isolated, such as silicon [27].

Many synthesis techniques have been described in the literature [20,28] in order to obtain low cost processes with high control over the structure, orientation and length of the produced CNTs. However, the most critical parameter in the resulting CNTs and thus, in their properties, is the choice of an adequate catalyst. They usually are transition metals [29,30] or bimetallic alloys, which improve the performance of classical catalysts [30–32].

The effective integration of a suitable and sensitive detection is one of the most important tasks in the development of miniaturized analytical devices, such as those named lab-on-a-chip. Electrochemical detection and grown CNTs, which follow a bottom-up fabrication scheme, have demonstrated to be a very convenient and

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promising alternative to conventional solid electrodes. They can be directly integrated in miniaturized devices and their dimensions are easily controlled, showing the convenience of this approach for electrode manufacture. Surfaces with very different properties can be achieved only with slight variations of CNTs synthesis procedure [33]. Therefore for a specific application a careful choice of the nanomaterial has to be made in order to obtain those with desired properties.

In this work we report and discuss about the influence of the orientation, density, underlayer deposition, or CVD reaction time on the grown CNTs properties (physical, electrochemical and analytical). The effect of these parameters was investigated by voltammetric and chronoamperometric measurements and dopamine (DA), an important catecholamine which is involved in Parkinson's and Alzheimer's diseases, was employed as electroactive redox molecule considering that it is easily converted to quinone by electrochemical oxidation. The carbon nanotubes electrodes were fabricated on glass substrates by means of chemical vapor deposition (CVD) and their performance has been compared to this presented on those conventional screen-printed carbon electrodes (SPCEs). Precision and surface stability over time have also been checked.

2. Materials and methods

2.1. Growth of MWCNTs by chemical vapor deposition (CVD)

Multiwall carbon nanotubes (MWCNTs) were grown by means of CVD in a commercial reactor (ET3000, FirstNano, CVD Equipment Corp., U.S.A.) onto Corning-glass substrates (Corning Inc., U.S.A.). With this purpose substrates were placed in a quartz tube at atmospheric pressure inside the furnace, in which the process gases (argon, hydrogen, and ethylene) were introduced in a controlled way.

For spaghetti-like MWCNTs synthesis, 40 mg of iron nitrate (Iron (III) nitrate monohydrate, 98%, Aldrich), 30 mg of alumina (Aeroxide Alu C, Evonik) and 3 mg of a molybdenum salt (Bis(acetylacetonato)-dioxomolybdenum (VI), Aldrich) were added in 30 mL of methanol, which is used to form a suspension and allow catalyst deposition. After sonication, the so-prepared liquid catalyst was spin-coated on the substrates at 2500 rpm for 30 s. Finally, the wafers were baked in an oven at 100 °C for 30 min, evaporating methanol and fixing the catalyst to the surface.

On the other hand, forest-like CNTs were grown from a Fe thin-film (5 nm) thermally evaporated in a Pfeiffer system (Classic 500) under high vacuum conditions (10^{-5} mbar). The same procedure was followed for underlayered substrates (Fe/ITO and Fe/Al), in this cases a thin layer of ITO (200 nm) or Al (5 nm) was deposited onto Corning glass surfaces prior to catalyst deposition.

After catalyst deposition, substrates were first annealed at 600 °C for 15 min under hydrogen atmosphere, generating Fe nanoparticles in both kinds of samples, and then hydrogen, argon and ethylene were flowed through the reactor chamber at a 1/1.6/0.3 rate. Finally, MWCNTs were grown at 750 °C for 30 min and the substrates were cooled to room temperature under an Ar flow of 0.3 slpm, obtaining both desired spaghetti and forest-like configurations on glass wafers.

2.2. Electrochemical measurements

Surfaces were electrochemically characterized by cyclic voltammetry and chronoamperometry.

Cyclic voltammetry was performed using a three-electrode configuration (working, reference and auxiliary), in which an Autolab PGSTAT 10 (ECO Chemie, The Netherlands) bipotentiostat was

controlled by Autolab GPES 4.9 version for Windows 98. The grown MWCNTs (spaghetti and forest) surfaces were used as working electrodes (WE), Ag/AgCl as reference electrode (RE), and a Pt wire as auxiliary electrode (AE) (Figure in supplementary data). The working area was delimited with an adhesive tape of 3 mm in diameter; notice that no leakage is produced between the tape and substrate, ensuring that there is no area fluctuation between electrodes. Cyclic voltammetry measurements were performed between 0 and 1.1 V at a scan rate of 100 mV s⁻¹. Screen-printed carbon electrodes (SPCE, Dropsens, Oviedo, Spain) were previously modified by 5 µL of 0.1 mg mL⁻¹ MWCNTs dispersion in DMF/H₂O [34].

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Chronoamperometry were carried out with the same software and computer. Measurements of the anodic current at constant potential (+0.7 V) were recorded for 100 s.

3. Results and discussion

3.1. CNTs growth procedure

The choice of an adequate substrate on which CNTs are going to be grown is one important parameter. It provides a solid foundation and must be able to inhibit the catalyst particles mobility [30]. Therefore, for the development of this work glass wafers were chosen as an ideal candidate due to their large area capability, robustness and low cost [35], particularly Corning-glass. This type of glass provides an upper limit of serviceability, as it is capable of withstanding higher temperatures (890 °C) than other glasses like soda-lime (473 °C) or borosilicate (521 °C). Fig. 1 shows a schematic diagram of the procedures followed in MWCNTs growth (details regarding with the CVD process are described in Section 2).

In this work, MWCNTs with different orientation (spaghetti and forest) have been grown with the assistance of two kinds of iron catalyst (liquid solution or sputtered thin-film). It is widely accepted that Fe and their compounds show the highest catalytic activity when compared to other transition metals [36]. For the spaghetti configuration (Fig. 1a), the liquid catalyst was prepared in methanol by suspension of iron nitrate (Fe acting as catalyst after undergoing a thermal treatment), alumina (catalyst seeds support), and a molybdenum salt (growth promoter). The resulting suspension was then deposited on the substrate by means of spin-coating. Finally, methanol was evaporated and the catalyst was fixed to the surface by baking the samples in an oven at 100 °C for 30 min. For forest the configuration a Fe thin film (5 nm) catalyst was obtained by thermal evaporation (Fig. 1b). In both cases after the CVD process, MWCNTs morphology was examined by field emission scanning electron microscopy (FE-SEM). From the micrographs it can be concluded that well-aligned forest-like MWCNTs of approximately 100 µm in height and homogeneous diameters comprised between 10 and 15 nm had been obtained.

The first measures made on bare surfaces show significantly lower signals for spaghetti configuration than for forest one (Fig. 2). In view of these results, it was decided to increase the spaghetti-like MWCNTs density on the surface. Thus, catalyst suspension was deposited onto substrates by means of drop-casting, obtaining (after the CVD process) high-density spaghetti carbon nanotubes. On the other hand and concerning the forest configuration, Fe catalyzed MWCNTs were not stable with time and after several measures no signal was observed. To overcome this problem and improve forest-like carbon nanotubes adhesion to the substrate, a thin film underlayer of 5 nm Al or 200 nm indium-tin-oxide (ITO) [37–39], which isolate glass from the active catalyst, was deposited onto glass wafer prior to Fe thermal evaporation (Fig. 1c). The catalyst was then deposited, and wafers were introduced into a CVD

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