

Carbon nanofiber vs. carbon microparticles as modifiers of glassy carbon and gold electrodes applied in electrochemical sensing of NADH

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Abstract

Carbon materials (CMs), such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), and carbon microparticles (CMPs) are used as doping materials for electrochemical sensors. The efficiency of these materials (either before or after acidic treatments) while being used as electrocatalysts in electrochemical sensors is discussed for β -nicotinamide adenine dinucleotide (NADH) detection using cyclic voltammetry (CV). The sensitivity of the electrodes (glassy carbon (GC) and gold (Au)) modified with both treated and untreated materials have been deeply studied. The response efficiencies of the GC and Au electrodes modified with CNF and CMP, using dimethylformamide (DMF) as dispersing agent are significantly different due to the peculiar physical and chemical characteristics of each doping material. Several differences between the electrocatalytic activities of CMs modified electrodes upon NADH oxidation have been observed. The CNF film promotes better the electron transfer of NADH minimizing the oxidation potential at +0.352 V. Moreover higher currents for the NADH oxidation peak have been observed for these electrodes. The shown differences in the electrochemical reactivities of CNF and CMP modified electrodes should be with interest for future applications in biosensors.

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1. Introduction

Carbon materials (CMs), such as graphite/carbon microparticles (CMPs), carbon nanotubes (CNTs), and carbon nanofibers (CNFs) have shown significant improvements in the development of novel sensors and biosensors [1–5]. High-surface area of CMs may also lead to new signal transduction processes [6,7] and to increased sensitivity in sensing applications [8–10].

Various processes used to be involved within a (bio)sensor system. These ranges from the analyte recognition, catalytic conversion, oxidation–reduction processes, mediation of electron

transfer, and finally the signal transduction and data display. To achieve a smooth running of the above processes a careful evaluation of the properties of the materials, ensuring an efficiency of their electrochemical properties, while incorporating them into the biosensor membranes must be considered. A better interaction and communication between the biomolecule and the transducer is also aimed to be achieved while using these materials. Only under these conditions a biosensor device will provide analytically useful information.

In recent years, with the great progress made in nanoscience and nanotechnology, interest is increasing in exploring the unique properties and potential technological applications of various nanostructures [11,12]. Many nanomaterials, such as peptide nanotubes [11], poly(1,2-diaminobenzene) nanotubules [13], and TiO₂ nanostructured films [14], particularly carbon nanotubes (CNT) [15–17], have been devoted to decreasing the high-overpotential for β -nicotinamide adenine dinucleotide

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(NADH) oxidation, minimizing surface fouling, and improving electron-transfer kinetics. Depending on the size, shape, and internal structure, nanoparticles frequently display unique physical and chemical properties [18].

CMP represents a highly ordered form of carbon. It is a solid that possesses delocalized π electrons on the basal planes, and this property imparts a weak basic character to the material in which the polarity can be manipulated by selected chemical treatments [19]. Carbon nanofibers (CNFs) represent carbon fibers with a nanometer-size diameter and no hollow core, but with many edge sites on the outer wall [20]. It has been recognized as one of the very promising materials based on its nanostructure and particular properties [21] and is expected to be used in various applications such as catalysts or catalyst supports [22], probe tips [23], and fuel cells [24].

Although there is a large amount of size overlap between CNT and CNF, there are significant structural differences. CNF consist of graphitic layers that stack either at an angle, perpendicular or parallel to the tube axis [25–28] while the CNT represent two single-walled and multi-walled structures. Single-wall CNTs (SWCNTs) comprise of a cylindrical graphite sheet of nanoscale diameter capped by hemispherical ends. The multi-wall CNTs (MWCNTs) comprise several to tens of incommensurate concentric cylinders of these graphitic shells with a layer spacing of 0.3–0.4 nm. MWCNTs tend to have diameters in the range 2–100 nm. The MWCNT can be considered as a mesoscale graphite system, whereas the SWCNT is truly a single large molecule [5].

Due to the unique characteristics of CNF there is a wide range of applications. The thermal and chemical stability, high-surface area, low-ohmic resistance, and the surface properties are the unique qualities that are exploited when CNF are used as catalytic support materials [25–30]. The surface at the tip of a CNF possesses a large amount of exposed edges due to the arrangement of the graphitic layers [31].

Recently, Wu et al. [32] studied the excellent catalytic activity of soluble CNF with good dispersion, to the oxidation of NADH for biosensing application. They show as the edge plane sites and oxygen-rich groups presented on the CNF surface could be partially responsible for its electrocatalytic behavior, which induced a substantial decrease by 573 mV in the overpotential of NADH oxidation reaction (compared to a bare glassy carbon electrode).

CNFs lead to more facile electron transfer [33] compared to CMPs. The solubility of CNF in dimethylformamide (DMF) facilitates its manipulation, including the coating on electrode surfaces for electrochemical biosensing applications, because the insolubility of carbon materials in most solvents is a major obstacle in implementing their widespread use [34].

In this work, chemically treated and untreated carbon materials (CNF and CMP) were used as modifiers of glassy carbon and gold electrode surfaces. The objective was to compare their efficiencies for electrochemical oxidation of NADH while using cyclic voltammetry (CV). Interesting results with interest for future biosensing applications will be shown.

2. Experimental

2.1. Materials and reagents

Herringbone graphite nanofibers, CNFs (100 nm in width and up to 10 μ in length) were purchased from catalytic materials. Graphite powder (carbon microparticle, CMPs, size 50 μ m) was obtained from BDH, UK. Further purification of carbon material was accomplished by stirring the CMs in 2 M nitric acid (PanReac, Spain) at 25 °C for 24 h [35]. A 0.7 mg of carbon material (CMP or CNF) was dispersed in 700 μ L of dimethylformamide (DMF, from Sigma–Aldrich). β -Nicotinamide adenine dinucleotide reduced form (NADH), potassium dihydrogen phosphate, potassium hydrogen phosphate, and sodium hydroxide were obtained from Sigma–Aldrich (Spain). The working solutions (NADH) were prepared daily by dilution in 0.1 M phosphate buffer at pH 7.0 with ultra pure water from a Millipore-MilliQ system.

2.2. Apparatus

Scanning electron microscopy (SEM, Hitachi S-570, Tokyo, Japan) was used to study the morphology of the electrode surfaces. Transmission electron microscope (TEM) images of the carbon materials were obtained using a Hitachi H-7000 (Hitachi Ltd., Tokyo, Japan). Scanning electron microscopy JEOL JSM-6300 (SEM, JEOL Ltd., Tokyo, Japan) with microanalysis equipped by an X-ray energy dispersive spectrometer (EDS) (Link ISIS-200, England) was used in order to evaluate the amount of chemical impurities (remained from their synthesis) and of oxygen groups introduced during the treatment of CMs with HNO₃.

The electrochemical measurements were performed with an electrochemical analyzer CHI 630B (CH Instruments) connected to a personal computer. The measurements were carried with a typical cell of 10 mL at room temperature (25 °C), using a three-electrode configuration. A platinum electrode and Ag/AgCl were used as counter and reference electrode, respectively. The glassy carbon (GC) and gold (Au) electrodes, with diameter of 2 mm, were from CH Instruments (Austin, TX, USA). The GC or Au modified electrodes using CNFs or CMPs suspended in DMF were also used as working electrodes. Modified electrodes were prepared in our laboratory according to the procedure described below.

2.3. Modification of GC and Au electrode surfaces

CNF and CMP were purified prior to use by a 2 M nitric acid solution. The bare electrodes (GC and Au electrodes) were polished with alumina paper (polishing strips 301044-001, Orion, Spain) and washed with water. These electrodes were then used for further modifications with CMs dispersed into DMF. Usually 0.7 mg CMs (treated or untreated) were mixed/dispersed into 700 μ L of DMF by ultrasonic agitation for about 1 h. After, 10 μ L of CMs–DMF solution were dropped directly onto of GC and Au electrode surfaces and allowed to dry at 40 °C for 45 min. Finally the electrodes were washed with water, and were ready

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