



A carbon nanotube/poly [Ni-(Protoporphyrin IX)] composite for amperometric detection of long chain aliphatic amines



Romina Carballo¹, Ana L. Rinaldi, Paula C. Dabas, Irene N. Rezzano^{*,1}

IQUIFIB, National Research Council (CONICET), Faculty of Pharmacy and Biochemistry, University of Buenos Aires, Junin 956, CP 1113 Buenos Aires, Argentina

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ABSTRACT

Poly [Ni-Protoporphyrin] film (pNiPP), containing multiwall carbon nanotubes (MWCNT) was used to cover a glassy carbon electrode. The hybrid material (pNiPP/MWCNT) successfully combines the permselectivity of pNiPP with the high conductivity of MWCNT.

The modified electrode was used to perform amperometric detection of long chain aliphatic amines (LCAA) in order to prevent the passivation effect of the aliphatic chain. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) demonstrated that the pNiPP/MWCNT facilitates the electron transfer reaction. The charge transfer resistance (R_{ct}) values were significantly lower by up to one order of magnitude compared to the bare electrode. Differential pulse polarography (DPP) showed a marked decrease of the overpotential generated by the aliphatic chain. The calibration of the amperometric peak area vs. concentrations of derivatized LCAA exhibits a linear response within the range of 0.018 and 28 μM and correlation coefficient (R^2) higher than 0.999 ($n = 5$). The quantitation limit of the pNiPP/MWCNT electrode is about 400 times lower than the UV–visible detection. RSD of 7.2%, 5.8%, 2.5% and 2.3% was obtained for concentrations of 0.028, 0.28, 2.8 and 28 μM of ferrocenyl octadecylamine. A solution of sphingosine, 0.23 μM , was exclusively detected with HPLC-ECD with pNiPP/MWCNT electrode.

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1. Introduction

In the last years, the development of nanostructured conducting polymers has received great attention because of their unique electronic, optical, and mechanical properties that make them versatile high conductivity materials [1]. In this regard, many electrochemically synthesized composites of conducting polymers and carbon nanotubes have shown better mechanical integrity, and higher electronic and ionic conductivity along with larger electrode specific capacitance [2].

Metalloporphyrins are ubiquitous organometallic compounds with interesting physicochemical properties that have been used in numerous electronic and electrochemical devices [3–5]. Therefore, the interaction between porphyrins and nanotubes becomes a very attractive area of research due to the promising optical and electronic properties of the resulting hybrid nanomaterials. A non-covalent wrapping of carbon nanotubes with porphyrins by condensation of formylporphyrins and pyrenes was reported [6]. The porphyrin ring is bonded to the nanotube wall by Van der Waals forces, and the π – π orbital interaction of the porphyrin ring and graphite surface enables the electronic charge transfer [7]. Polymeric bimetallic Fe(III) and Cu(II) porphyrin films were

deposited onto multiwalled carbon nanotubes (MWCNT). The method generates stable and homogeneous dispersion of nanotubes in the polymer, favoring the catalytic reduction of hydrogen peroxide [8].

Also, the electrochemical behavior of electrodes modified with Ni(II) Protoporphyrin films was studied. This film does not show significant catalytic properties but deposited onto a glassy carbon electrode behaves as a permselective conducting film with non-Faradic current response proportional to ion concentration in flow injection analysis [9]. This response resulted highly dependent of the electrode potential, which produces positive charges in the film counterbalanced by the movement of ions.

The structural units of the sphingolipids are long-chain aliphatic amines containing two or three hydroxyl groups and often a distinctive *trans*-double bond. The main component in nature is C18, but there are also small amounts of C16 to C19 dihydroxy bases. Sphingolipids have important roles in membrane and in cell regulation as second messengers for growth and differentiation factors [10]; therefore, the development of sensitive and reliable techniques to achieve the simultaneous quantification of different sphingoid bases is a relevant matter.

The most commonly used method to quantify sphingolipids is HPLC with different detectors (UV–vis, fluorometric, amperometric). These detectors require the presence of chromophoric, fluorophoric or redox groups in the analyte which are absent in the aliphatic amines. Several studies focused on the detection of low molecular weight aliphatic

* Corresponding author.

E-mail address: irezcano@ffyb.uba.ar (I.N. Rezzano).

¹ CONICET permanent staff.

amines, employing a series of aromatic reagents that generate fluorescent [11–14] or chemiluminescent labels [15].

The ferrocene (Fc) molecule is one of the most stable and versatile organometallic compounds and has therefore been used as an electroactive component for the construction of redox molecules with various applications (biosensors [16], electrochemical probes [17] and catalysis [18]). Even though the reduction potential is highly dependent on the electronic nature of the substituents [19], the cyclic voltammetry maintains the reversible ferrocene/ferrocenium ion (Fc/Fc⁺) redox peak.

As far as we know, few studies have addressed long chain aliphatic amines derivatized with ferrocene [20] probably because the long chain aliphatic amines not only generate an electrode/solution interface with different electrical properties, but also aggregate and adsorb onto the electrode surface [21]. Thus, the supramolecular structures generate a hydrophobic environment which diminishes the charge transfer process.

In this paper, we explore a hybrid nanomaterial (pNiPP/MWCNT) to perform the amperometric detection of long chain aliphatic amines containing the ferrocenyl unit. The combination of the permselectivity of poly [Ni-(Protoporphyrin IX)] films with the electronic properties of the carbon nanotubes results in a composite that overcomes the passivating effect of aliphatic amines.

2. Experimental

2.1. Materials

Ni-Protoporphyrin IX (NiPP) was prepared according to standard procedure [22].

Tetrabutylammonium perchlorate (TBAP) was obtained by precipitation of a saturated solution of the tetrabutylammonium hydroxide with perchloric acid, twice recrystallized from ethanol, and dried under vacuum. *Caution! Perchlorate salts may be explosive. It should be handled with care and in small amounts.*

Multiwalled carbon nanotubes (MWCNT) (diameter 15 ± 5 nm; length 1–5 μ m) were purchased from Nano-Lab and used without further purification.

Ferrocene carboxaldehyde (CHOFc) 98%, ferrocene methanol (FcOH) 97%, sodium borohydride, lithium perchlorate, D-sphingosine (d 18:1) (Sph) and hexadecylamine (HDA) 98% were of analytical grade (Sigma). Octadecylamine (ODA) was purchased from Fluka. All other reagents were of analytical grade. Deionized water was used for all aqueous solutions. All solutions were filtered through a 0.45 μ m nylon membrane (Micron Separations Inc., Westborough, MA, USA) and degassed before use.

2.2. Apparatus

Cyclic voltammeteries (CVs) and amperometric detection were performed with a purpose built potentiostat (TEQ-Argentina), with digital signal generator for implementation of different electrochemical techniques. Electrochemical impedance spectra were recorded using a potentiostat TEQ4-Z (TEQ-Argentina) and a frequency response analyzer. Data analysis was performed with the program ZView (Scribner Associates, USA). A glassy carbon working electrode (0.25 cm² area), an Ag/AgCl KCl 3 M reference electrode (BAS) and a platinum wire auxiliary electrode were used for voltammetric, differential pulse polarography, and electrochemical impedance experiments. A purpose built Teflon cell was used in impedance measurements.

An HP8452 diode array spectrophotometer and a quartz crystal cell were used to obtain the UV spectra.

The scanning electron micrographs of the polymers were obtained using a Zeiss DSM982 GEMINI SEM with Field Emission Gun (FEG) and operated at 3 kV.

2.3. Electrochemical measurements

All electrochemical experiments were carried out in acetonitrile:methanol (70:30) with 0.1 M LiClO₄. The scan rate range in cyclic voltammetric (CV) was 0.001 V s⁻¹ to 1 V s⁻¹.

A frequency range of 100 kHz to 0.1 Hz was used for impedance spectroscopic (EIS) measurements. The amplitude of oscillation was set to 10 mV and the working potential to +0.500 V.

Differential pulse polarography (DPP) experiments were carried out using a potential ramp starting at 0.0 V and going up to 1 V in a pulsed manner. The following experimental parameters were employed: potential step = 0.5 mV, pulse width = 0.06 s, pulse amplitude = 50 mV, and pulse period = 0.2 s.

2.4. Preparation of the modified electrodes

The glassy carbon electrode was polished with 0.3 and 0.05 mm diameter alumina particles and finally rinsed with deionized water. One milligram (1 mg) of MWCNT was ultrasonically dispersed in 4 mL of 3 mM NiPP solution before electropolymerization.

The electropolymerization of pNiPP/MWCNT onto the electrodes was carried out in 0.1 M TBAP/CH₂Cl₂ by potential sweep between 0.00 and +1.80 V (vs. Ag/AgCl) at 0.05 V s⁻¹, five cycles. Then, the film was oxidized by cycling between -0.2 and +1.80 V in aqueous 50 mM KH₂PO₄ solution.

After polymerization the resulting solution was centrifuged during 20 min at 3000 g. Once the supernatant was discarded, the solid was re-suspended to obtain the UV-vis spectra of the pNiPP/MWCNT.

2.5. HPLC measurements

The HPLC equipment consisted of a Waters 1525 Binary HPLC pump, a Rheodyne injection valve (Model 7125) with a 50 μ L sample loop, a guard column and a reversed phase column, a flow cell for amperometric detection (BAS), and 2487 Dual k Absorbance detector (Waters).

Separation was achieved using a Luna 5u C18 Phenomenex (150 mm \times 4.6 mm i.d., 5 μ m particle size); the isocratic mobile phase was acetonitrile:methanol (70:30) with 0.1 M LiClO₄ and the flow rate 1.0 mL min⁻¹.

Amperometric detection was performed with a microprocessor controlled electrochemical analyzer. The 7 μ L thin layer electrochemical cell consisted of a dual glassy carbon working electrode (7 mm² working area), Ag/AgCl reference electrode (BAS), and a stainless steel auxiliary electrode. The measurements were carried out at +0.500 V after allowing the transient current to decay to steady state before analysis.

UV detection was performed at 272 nm.

2.6. Preparation and quantification of standard solutions

Ferrocenyl derivatives, FcODA, FcHDA and FcSph, were synthesized and characterized according to the procedure described in the supplementary information.

Standard stock solutions (2.8 mM) of ferrocenyl octadecylamine (FcODA), ferrocenyl hexadecylamine (FcHDA), and ferrocenyl sphingosine (FcSph) were prepared by separately dissolving 13.2 mg, 12.8 mg and 14.2 mg of each compound, respectively, in 10 mL of methanol. Working standard solutions (280, 28, 2.8, 1.4, 0.7, 0.35, 0.28, 0.18 and 0.018 μ M) were prepared by diluting the standard solution with methanol.

The chromatographic peak areas were employed to quantify each analyte. Linearity, limits of detection (LODs), and limits of quantitation (LOQs) were compared for the three methods employed: HPLC-UV, and HPLC-ECD with and without pNiPP/MWCNT.

The calibration curves were constructed and treated with linear least square regression analysis. The analytical sensitivity (γ), the most adequate parameter to compare different instrumental methods, is calculated as $\gamma = SEN/s_y$, where s_y is a convenient measure of noise

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