



Exploiting charge/ions compensating processes in PANI/SPANI/reduced graphene oxide composite for development of a high sensitive H₂O₂ sensor



Edmilson Tinoco Vilela Jr.^a, Rita de Cássia Silva Carvalho^b, Sakae Yotsumoto Neto^b,
Rita de Cássia Silva Luz^b, Flavio Santos Damos^{b,*}

^a Department of Chemistry, Federal University of Jequitinhonha and Mucuri's Valleys, 39100-000 Diamantina, MG, Brazil

^b Department of Chemistry, Federal University of Maranhão, 65080-805 São Luís MA, Brazil

ARTICLE INFO

Article history:

Received 20 March 2015

Received in revised form 6 June 2015

Accepted 6 June 2015

Available online 9 June 2015

Keywords:

Cytochrome c

Polyaniline

Sulfonated polyaniline

Graphene

Hydrogen peroxide

Scanning electrochemical microscopy

ABSTRACT

The present work describes the development of a polyaniline/polyaniline-2-sulfonic acid/reduced graphene oxide composite (PANI/SPANI/rGO) modified electrode by electropolymerization to detection of hydrogen peroxide. The ionic transport at the PANI/SPANI/rGO film was evaluated by the investigation of the protonic and anionic participation in the charge compensation processes. The sulfonic group and reduced graphene oxide in the composite film contribute to suppression of the anionic transportation and improve the composite ability to fixing cytochrome c redox protein (Cyt c). The ability of the PANI/SPANI/rGO film in absorbing the Cyt c resulted in a high sensitivity ($0.45 \mu\text{A L} \mu\text{mol}^{-1}$), high linear range (from $0.1 \mu\text{mol L}^{-1}$ up to $1000 \mu\text{mol L}^{-1}$) and low limit of detection ($0.04 \mu\text{mol L}^{-1}$) to hydrogen peroxide. Indeed, the hybrid organic-inorganic sensor exhibited a good reproducibility and stability to H₂O₂ reduction at an applied potential of $-200 \text{ mV vs. Ag/AgCl}$.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Intrinsic conducting polymers (ICPs) are also knowledge as “synthetic metals” due to their unique electrochemical, magnetic and optical properties inherent to metals conductors [1–3]. In this sense, the ICPs have been widely exploited in the development of corrosion protecting films, capacitors and (bio)sensors [4]. In the last one application, the ICPs can act as an active template to biological element immobilization due to their ability to charge transport and biocompatibility [5–7].

Nowadays, a number of monomers and its derivatives have been exploited in fabrication of conducting polymers, including pyrrole, thiophene, polyaniline, and its derivatives [8]. Among then, polyaniline (PANI) and its derivatives have received high attention due to their unique properties including facile synthesis, good electrical conductivity, and electrochemical stability [9]. PANI can provide a suitable environment for the immobilization of biomolecules ensuring an excellent accessibility to the catalytic sites providing a spatial orientation of the biomolecules for facilitating its interaction with the target [10]. In addition, the PANI modified

electrodes have shown impressive signal amplification and elimination of the signal from the electrode fouling [11].

Aniline based polymer films exhibits two redox couples which can facilitate the redox protein electrochemical processes. However, the PANI also exhibits dramatic changes in its electronic structure and physical properties with protonating state because its conductivity depends on the protonation of polyemeraldine base. According to the literature [12], the PANI redox activity is more pronounced at solution pH not exceeding 3 or 4.

The investigation of charge compensation processes of self-doped polyanilines by Torresi's research group [13] has shown the viability in control of dopant nature in PANI-derivatives based films. In this sense, the self-doped polyaniline (SPANI) is an alternative material with high activity over a wide range of pH values since it shows a negatively charged functional group which acts as an inner dopant anion attached to the polymer structure. Therefore, the self-doped polyanilines can suppress the anion activity, which occur between the polymer and surroundings, during oxidation and reduction processes [14].

However, the electrical conductivity of polyaniline decreases with the sulfonation process due to the withdrawal resonant effect of the sulfonic acid groups which withdraws electrons from the benzene ring and decreases the electron density at the polyaniline

* Corresponding author.

E-mail address: flavio.damos@ufma.br (F.S. Damos).

backbone [14]. Thus, the self-doped polyanilines shows lower electrical conductivity in comparison to dedoped polyaniline which limits the application of sulfonated polyanilines in the development of biosensors [15].

In nowadays, the introduction of conductive inorganic materials based on carbon has attracted a high interest as doping material in organic conducting polymers. Among the carbon based materials, the reduced graphene oxide (rGO) has attracted considerable attention due to its unique structural, mechanical and electronic properties [16,17]. In this sense, the conducting polymers doped with rGO have shown impressive mechanical, electrical, photonic, and optical properties [18]. A number of research groups have shown that the reduced graphene oxide improves the mechanical and electrochemical performance of several polymeric matrices [19]. The first successful evidence of association between PANI and graphene in sensors development has opened a promising field of application to organic–inorganic composites to detection of several analytes [20]. Therefore, the development of PANI/SPANI/rGO composite materials can provide a high control of doping/dedoping processes in organic–inorganic composite, contributing for chemical, electrical and structural polymer flexibility which improves the adsorption and incorporation of biomolecules [21].

Hydrogen peroxide monitoring is of high importance in many research areas such as environmental, food safety, industrial analysis, and biological systems. In this sense, the development of methods for the detection of H_2O_2 with high sensitivity, wide linear range, and selectivity is of high interest for the practical purpose [22]. A number of analytical techniques [23–26] have been applied for the determination of H_2O_2 , however they lack fast response, low cost and portability possibilities [27].

This work describes the development of an efficient platform based on PANI, SPANI and reduced graphene oxide for immobilizing cytochrome c to the high sensitive H_2O_2 detection. The ions compensating processes in PANI/SPANI/rGO nanocomposite were investigated with the purpose of controlling the amount of cytochrome c (Cyt c) in the composite.

2. Experimental

2.1. Reagents, materials and procedures

All chemicals were of analytical grade. The graphite powder and aniline-2-sulfonic acid were purchased from Sigma, St. Louis, USA. Disodium and monosodium phosphates (Na_2HPO_4 and NaH_2PO_4) were acquired from Synth, São Paulo, Brazil. Aniline (98%) from Aldrich (Milwaukee, USA) was distilled prior to use. The aniline aqueous solution was stored in a dark flask at low temperature. Sulfuric acid (H_2SO_4) from Synth and hydrogen peroxide (H_2O_2) acquired from Merck were used as received. The graphite oxide (GO) and reduced graphene oxide (rGO) were prepared by a modification of Hummers and Offeman's method from graphite powders (Bay carbon, SP-1) [28–30]. Deionized water was used after purification in a Purelab from ELGA and the actual pH of the buffer solutions was determined with a pH/Temperature meter from Digimed. The quartz crystals with AT-cut and fundamental frequency of 6 MHz were acquired from Metrohm Autolab B. V., The Netherlands.

2.2. Preparation of PANI/SPANI/rGO/Cyt c modified electrode

The preparation of PANI/SPANI/rGO modified electrode was carried out in a dispersion containing 1 mg mL^{-1} reduced graphene oxide, 0.05 mol L^{-1} aniline, 0.05 mol L^{-1} aniline-2-sulfonic acid, and 0.1 mol L^{-1} sulfuric acid by sweeping the electrode potential between -0.1 V and 1.1 V . After this step, the cytochrome c redox

protein immobilization on the modified PANI/SPANI/rGO composite was carried out by adapting the method previously described by Yang and Mu [31]. Briefly, the PANI/SPANI/rGO modified electrode was transferred into the Cyt c solution (2 mg mL^{-1} and pH 5.5) and 500 mV vs. Ag/AgCl was applied to the electrode for 20 min to immobilize Cyt c in the organic–inorganic composite. The Cyt c was stabilized in the PANI/SPANI/rGO by dropping a 2.5% (v/v) glutaraldehyde solution to form the covalent linkages between the Cyt c and the composite backbone [32].

2.3. Electrochemical, EQCM, and SECM measurements

Cyclic voltammetry, amperometry, electrochemical impedance spectroscopy and quartz crystal microbalance experiments were carried out with a Potentiostat/Galvanostat AUTOLAB 128N equipped with EQCM and FRA2 modules. The impedance data were analyzed by non-linear least squares using the EQUIVCTR.PAS program by Boukamp [33]. The electrochemical impedance spectra were carried out with a sinusoidal potential modulation of 10 mV superimposed on a fixed d.c. potential and the responses were recorded from 100 kHz up to 0.1 Hz .

The scanning electrochemical microscopic measurements were carried out with a CHI 920C microscope from CH Instruments, Inc (Austin, USA). SECM measurements were carried out with a four-electrode electrochemical cell built in Teflon with a 10 mm diameter aperture. Microelectrodes of Pt with radius of $5 \mu\text{m}$ and RG ~ 5 were employed as tip in SECM measurements.

3. Results and discussion

3.1. Electrochemical performance of PANI/SPANI/rGO composite film

The potentiodynamic growth of the PANI/SPANI/rGO film was carried out in an electrolytic solution consisting of 0.05 mol L^{-1} aniline, 0.05 mol L^{-1} aniline-2-sulfonic acid, 1 mg mL^{-1} reduced graphene oxide and 0.1 mol L^{-1} H_2SO_4 by potential scanning between -0.1 and 1.1 V at 50 mV s^{-1} .

During the first anodic scan in Fig. 1 a high change in the current can be seen in the potential range of 0.5 up to 1.1 V . On the other hand, the frequency of the QCM crystal does not show changes until 0.75 V vs. Ag/AgCl. On the cathodic scan, the frequency decreases until about 0.75 V and then remained constant until the end of the cathodic scan. The frequency change delay in

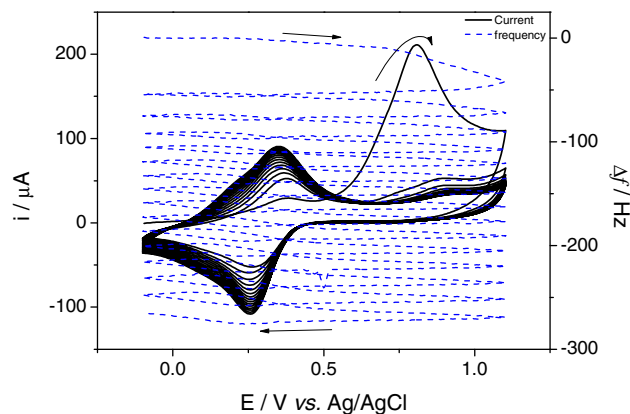


Fig. 1. Cyclic voltammograms (black line, left axis) and corresponding frequency vs. potential curves (blue line, right axis) recorded during potentiodynamic growth of the PANI/SPANI/rGO film in a solution containing 0.05 mol L^{-1} of aniline, 0.05 mol L^{-1} of aniline-2-sulfonic acid, 1 mg mL^{-1} reduced graphene oxide, and 0.1 mol L^{-1} H_2SO_4 . Scan rate: 0.05 V s^{-1} . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

<https://daneshyari.com/en/article/218146>

Download Persian Version:

<https://daneshyari.com/article/218146>

[Daneshyari.com](https://daneshyari.com)