



Electrochemical sensor based on reduced graphene oxide modified with palladium nanoparticles for determination of desipramine in urine samples



Fernando H. Cincotto^b, Diego L.C. Golinelli^a, Sergio A.S. Machado^b, Fernando C. Moraes^{a,*}

^a Chemistry Department, Federal University of São Carlos, São Carlos, SP, Brazil

^b Institute of Chemistry of São Carlos, University of São Paulo, São Carlos, SP, Brazil

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ABSTRACT

A nanostructured material based on palladium nanoparticles supported over reduced graphene has been synthesized, characterised and applied on the sensitivity analysis of antidepressant in urine samples. The morphology, structure, and electrochemical performance of the sensors were characterised by field emission gun scanning electron microscopy, X-ray diffraction, and cyclic voltammetry. The antidepressant quantification process was based on the reversible electrode oxidation of the electrochemically produced desipramine dimer, that appeared as oxidation process at +0.11 V. Differential pulse voltammetry in phosphate buffer solution at pH 7.0 allowed the development of a method to determine desipramine levels in the range of 0.3–2.5 $\mu\text{mol L}^{-1}$, with limit of detection (LOD) estimated at 1.04 nmol L^{-1} (0.31 $\mu\text{g L}^{-1}$). The system was suitable on the detection of desipramine in urine samples.

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1. Introduction

According to the World Health Organisation, on a global scale, more than 350 million people are affected by mood disorders, especially depression [1]. There are two types of depression that can be long-lasting or recurring. These types can manifest as several cases leading to suicide, or mild depression cases can be treated without drugs. However, in several moderate or severe cases, patients need medication and professional treatment [2]. Antidepressants can be classified into five groups, which are: tricyclic, related tricyclics, selective serotonin reuptake inhibitors (SSRIs), monoamine oxidase inhibitors (MAOIs), and atypical, which cannot be accommodated in any of the other classes [3,4].

Tricyclic antidepressants such as desipramine have a mechanism of action in the pre-synaptic level that blocks the reuptake of monoamines, especially norepinephrine, dopamine and especially serotonin. The postsynaptic activity involves blocking muscarinic receptors (cholinergic), histamine type-1, alpha-2, beta-adrenergic, antidepressant effect, but have side effects [5]. In clinical samples, it was reported that the desipramine toxic doses starts above

500 $\mu\text{g L}^{-1}$, in plasma with half-life between 12 and 28 h [6]. There are several reports correlating the tricyclic antidepressant overdoses with serious body disorders such as sleepiness, seizures, respiratory problems, and finally coma [7]. In this sense, the drug dosage in the organism must be extremely controlled.

The most used analytical methods for desipramine determination are based on liquid and gas chromatography [8,9], electrophoresis [10] and spectrophotometry [11]. The electroanalytical methods to detect desipramine are based on a two-step oxidation process. The first observed process maybe electrochemical oxidation of the nitrogen atom present on the heterocyclic ring that lead to a dimerization process as suggested by Tammari et al. [12]. In the reverse sweep (cathodic way), in acid media, it is possible to observe two electrochemical processes related to the electrochemical reduction of the product of dimerization reaction [13]. Based on this electrochemical behaviour, there are several works that report the use of an electroanalytical method to determine desipramine. Knihnicki et al. [14] proposed a voltammetric method based on glassy carbon electrode and gold screen printed electrodes to determine desipramine with a detection limit of 7.0 nmol L^{-1} . Sanghavi and Srivastava [15] developed a sensor based on Amberlite XAD-2 and TiO_2 nanoparticles (TNPs) modified glassy carbon paste electrodes to detect desipramine with a level at 0.43 nmol L^{-1} .

* Corresponding author.

E-mail addresses: fc Moraes@ufscar.br, fc Moraes@hotmail.com (F.C. Moraes).

One special material that can be used for the development of electroanalytical sensors is reduced graphene oxide (RGO). RGO has similar characteristics to graphene nanosheets, i.e., the singular two-dimensional structure is formed by a few layers of sp^2 carbon atoms, in a π -conjugated system leading to high electron mobility and fast charge transfer, allowing the appearance of an electrocatalytic effect [16]. In relation to graphene nanosheets the RGO can be easily obtained from graphene oxide reduction [17]. Also, the RGO exhibited an increase of the conductivity and electrocatalytic properties in relation to pristine graphene nanosheets [18]. Additionally, the RGO acts as a support for the immobilisation of several species that can be used as a platform for the development of biosensors and sensors, in which it can be cited: enzymes [19], DNA [20], biomarker [21], metallic oxides [22], quantum dots [23] and metallic nanoparticles [24]. In this sense, this study focuses on the synthesis, characterization and application of electrochemical sensors based on palladium nanoparticles (PdNPs) supported on RGO. This nanostructured material yielded excellent sensitivity for desipramine quantification, as well as a high electrocatalytic activity and a low detection limit. The proposed glassy carbon electrode modified with the material RGO/PdNPs is shown to be promising as a fast, simple and sensitive method to monitor the levels of antidepressant in urine.

2. Experimental

2.1. Chemicals and solutions

All used chemicals employed in this work were of analytical grade. Desipramine standard, uric acid, ascorbic acid, palladium chloride, sodium phosphate and sodium hydrogenphosphate was obtained from Sigma-Aldrich (Germany). The 0.1 mol L^{-1} of phosphate buffer solution (PBS) was used as a supporting electrolyte. All solutions were prepared with water purified in a Millipore Milli-Q system (resistivity $> 18.2 \text{ M}\Omega \text{ cm}$). Graphite powder ($< 20 \mu\text{m}$), sodium nitrate, sulphuric acid, nitric acid, and potassium permanganate, purchased from Sigma-Aldrich (Germany) were used for graphene oxide synthesis. Ethylene-glycol, purchased from Sigma-Aldrich (Germany), and acetone purchased from Synth (Brazil) were used in hydrothermal micro-wave assisted synthesis.

2.2. Apparatus and procedures

Cyclic voltammetry experiments (CV) were performed using a PGSTAT 302 Autolab electrochemical system (Eco Chemie, Netherlands) monitored with NOVA (Eco Chemie, Netherlands) software. A conventional electrochemical cell was assembled with three electrodes, in which a glassy carbon electrode (3.0 mm of diameter) modified with the (RGO/PdNPs) composite was used as a working electrode, an Ag/AgCl electrode in KCl (3.0 mol L^{-1}) as a reference electrode, and a Pt plate as an auxiliary electrode. The electrochemical behaviour of the desipramine on the proposed electrode were carried out using CV in 0.1 mol L^{-1} PBS (pH 7.0) at controlled temperature (25°C), in which the scans were collected in a potential range from -0.2 to $+1.1 \text{ V}$ with a scan rate of 25 mV s^{-1} . The analytical quantifications were obtained using differential pulse voltammetry (DPV) experiments in 0.1 mol L^{-1} PBS (pH 7.0) through sequential additions of desipramine standard solution aliquots, in a potential range from -0.2 to $+0.3 \text{ V}$, with a scan rate at 10 mV s^{-1} , pulse amplitude at 50 mV and a step potential at 2 mV . The morphologies of the RGO and RGO/PdNPs were examined using a field-emission gun scanning electron microscope (FEG-SEM) and the images were recorded using a model FEI Inspect F50 microscope (FEI Company, Hillsboro, USA).

2.3. Synthesis of graphene oxide

A Hummers method was used to prepare the graphene oxide (GO) [25]. For this, graphite powder (10.0 g) was mixing with sodium nitrate (10.0 g) and dispersed in 400.0 mL concentrated sulphuric solution (ratio 1:3 in volume of $\text{HNO}_3/\text{H}_2\text{SO}_4$). The mixture was kept in an ice bath with magnetic stirring. Then, KMnO_4 (50.0 g) was slowly added in the reaction flask and the mixture was left under vigorous stirring for 2 h. After, the synthesis temperature was controlled at 60°C , and the reaction was allowed to continue at this temperature by 30 min. Subsequently, 75.0 mL of H_2O_2 (30% v/v) was added in the system. After the solution becomes light brown, 1.0 L of HCl solution (10% volume) was added to the mixture, which was kept afterwards in a refrigerator at 4°C for 24 h. The light brown supernatant was collected and the GO was separated by centrifugation at 10,000 rpm and dried by lyophilisation for 24 h.

2.4. Synthesis of RGO/PdNPs and electrode preparation

The RGO/PdNPs composite was synthesized by suspending 100.0 mg of GO in 50.0 mL of ethylene-glycol. The suspension was kept in an ultrasonic bath for during 20 min. Then, 1.5 mmol L^{-1} of PdCl_2 was added in the reaction flask. The mixture was submitted to microwave-assisted hydrothermal treatment at 150°C for 30 min. Due to the microwave hot spots, the GO was thermally reduced to RGO and the Pd nanoparticles were obtained. Thus, an amount of 1.0 mg RGO/PdNPs was suspended in 1.0 mL of ethanol containing 0.5% Nafion. Thus, $10.0 \mu\text{L}$ of the composite suspension was dropped on the top of the glassy carbon (GC) plate (0.07 cm^2 of geometric area) and dried overnight in a desiccator.

3. Results and discussion

3.1. Morphological and structural characterisations

Morphological and structural characterisations were performed and the electrochemical profile of the prepared RGO/PdNPs was assessed in order to evaluate whether the composite synthesis procedures were effective in the palladium nanoparticles support over the RGO layers. Fig. 1A displays a typical FEG-SEM image of the recently prepared graphene oxide (GO) from the modified Hummers method [25]. It was possible to observe that the GO was not a single-layered structure, but was displayed as an overlap of a few layers with a considerable degree of transparency. However, it is evident that the GO was efficiently synthesized, because the Raman microscopy that demonstrated the classic characteristics of graphene (known as the graphene fingerprints), i.e., the D_{Band} at 1352 nm and G_{Band} at 1609 nm . It is possible to observe that the G_{Band} is more intense than the D_{Band} , with the I_D/I_G ratio for GO of 0.68, as expected to GO [26].

In the synthesis sequence, after the micro-wave assisted hydrothermal process, the Pd nanoparticles were effectively supported on the RGO surface, as presented in the micrographs of Fig. 1B. These nanoparticles are well-dispersed, with a narrow particle-size distribution. Using the Image Photo Pro Plus 6[®] software, different FEG-SEM images of the RGO/PdNPs were mapped and scanned, observing an average palladium particle size of $8.5 \text{ nm} \pm 1.9 \text{ nm}$. Additionally a Raman microscopy was performed in order to confirm that the RGO was successfully synthesized. In Fig. S1 (Supplementary information) the Raman spectra collected from the GO sample (black line), RGO (red line) are presented. The G and D bands at 1610 and

1360 cm^{-1} , respectively, are clearly observed. As expected for the GO sample, the G_{Band} is more intense than the D_{Band} . After the

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