Talanta 161 (2016) 333–341

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Electrochemical sensor based on graphene oxide and ionic liquid for ofloxacin determination at nanomolar levels

Ademar Wong [a], Tiago Almeida Silva [a], Fernando Campanhã Vicentini [b], Orlando Fatibello-Filho [a,*]

[a] Department of Chemistry, Federal University of São Carlos, 13560-970 São Carlos, SP, Brazil
[b] Center of Nature Sciences, Federal University of São Carlos, 18290-000 Buri, SP, Brazil

ARTICLE INFO

Article history:
Received 9 July 2016
Received in revised form
12 August 2016
Accepted 14 August 2016
Available online 15 August 2016

Keywords:
Graphene oxide
Ionic liquid
Ofloxacin
Nanomolar concentration
Carbon paste electrode

ABSTRACT

New insights into the design of highly sensitive, carbon-based electrochemical sensors are presented in this work by exploring the interesting properties of graphene oxide (GO) and ionic liquids (ILs). An electrochemical sensor based on the carbon paste electrode (CPE) modified with GO and IL was developed for the sensitive detection of ofloxacin using square-wave adsorptive anodic stripping voltammetry (SWAdASV). GO sheets were obtained from the acid treatment of graphene and characterized by scanning and transmission electronic microscopy (SEM and TEM) and selected area electron diffraction (SAED), and the electrochemical behavior of the modified GO-IL/CPE was explored by electrochemical impedance spectroscopy studies. The CPE modification with GO and IL allowed an 8.2 fold increase in the analytical sensitivity for ofloxacin sensing compared to the unmodified CPE. Under the optimized experimental conditions using the SWAdASV technique, the GO-IL/CPE sensor provided an analytical curve for ofloxacin in the concentration range of 7.0×10^{-9} to 7.0×10^{-7} mol L^{-1}, with a sensitivity of 7.7×10^{6} μA L mol^{-1} and limit of detection of 2.8×10^{-10} mol L^{-1} (0.28 nmol L^{-1}). The proposed sensor was successfully applied for the ofloxacin determination in human urine and ophthalmic samples, with recoveries near 100%. The results were similar those obtained by a spectrophotometric comparative method.

1. Introduction

Ofloxacin is a synthetic antibiotic used against gram-negative and gram-positive bacteria [1,2]. Its white crystalline powder form is generally recommended for people with urinary tract infections, prostatitis, lower respiratory tract infection and skin structure infections [3]. The extensive use of this drug can cause adverse effects such as tendon damage, peripheral neuropathy (which may be irreversible) and, in severe cases, it can result in lifelong disabilities [4]. The analytical determination of ofloxacin is very important for minimizing the risks of human intoxication and prevents serious environmental impacts, such as the development of resistant bacteria [5,6].

Analytical methods such as chemiluminescence [7], spectrofluorimetry [8], high performance liquid chromatography (HPLC) [9], capillary electrophoresis [10], spectrophotometry [11], and mass spectrometry [12] are utilized for the determination of ofloxacin. However, there are some disadvantages associated to the use of these methods, such as the large consumption of reagents, high cost of acquisition and maintenance of equipment, leading to a high cost of analysis. A way to overcome these disadvantages is the electrochemical monitoring of ofloxacin using chemically modified electrodes (CMEs). Several conducting or semiconducting materials are used as modifiers to increase the performance of CMEs. The materials widely used as electrode modifiers are: nanoparticles [13], ions [14], polymers [15], phthalocyanine and porphyrin complexes [16], carbon nanomaterials (*e.g.*, graphene and carbon nanotubes) [17,18], ionic liquids [19], and others.

Recently, CMEs based on graphene oxide (GO) and/or ionic liquids (ILs) have shown immense potential for the sensitive determination of target analytes. GO is a hydrophilic nanostructured carbon material obtained from graphene, dispersible in aqueous media owing to the presence of oxygen groups in its structure. It has received great attention due to its excellent physical and chemical properties such as high surface area, excellent conductivity, and high mechanical strength. Thus, GO has been used in a wide range of applications, including electronics [20], energy storage [21], batteries [22], fuel cells [23], biological systems [24] and electrochemical sensors and biosensors [25–28]. Ionic liquids

* Corresponding author.
E-mail address: bello@ufscar.br (O. Fatibello-Filho).

http://dx.doi.org/10.1016/j.talanta.2016.08.035
0039-9140/

are important materials that have also attracted much attention due to their unique physical and chemical properties such as high conductivity, wide potential window, high viscosity, low volatility, and chemical and thermal stability. Ionic liquids are formed by positively (cation) and negatively (anion) charged ions in the liquid phase [29]. The use of ILs as modifiers to electrochemical sensor surfaces increases the stability, sensitivity and selectivity of the oxidation and/or reduction of chemical compounds [30,31]. The modification of electrodes with ILs associated with nanomaterials such as graphene can be used to improve the catalytic and/or electrocatalytic activity and the heterogeneous electron transfer [32,33]. The numerous advantageous that can be achieved from the use of CMEs constructed using GO and ILs include accuracy, stability, reproducibility, high sensitivity and selectivity [34,35]. In the literature, there are some works employing CMEs based on nanomaterials to enhance detection, such as the study performed by Zhou et al. [33]. In that study, a glassy carbon electrode modified with graphene oxide-ionic liquid composites and gold nanoparticles was applied to the ultrasensitive electrochemical detection of Hg^{2+} [33]. Shan et al. [36] determined NADH and ethanol using a modified glassy carbon electrode based on an ionic liquid and functionalized graphene within a chitosan film . In another work, Sun et al. [37]. proposed a novel sensing platform based on graphene oxide, 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid and Nafion for the immobilization of hemoglobin (Hb). This sensor exhibited excellent electrocatalytic activity towards trichloroacetic acid and H_2O_2.

The aim of this work it was to develop an electrochemical sensor based on a carbon paste electrode modified with GO and IL for the sensitive voltammetric determination of ofloxacin at nanomolar levels.

2. Experimental

2.1. Reagents and solutions

Ofloxacin standard and 1-buthyl-3-methylimidazolium tetrafluoroborate (IL) were purchased from Sigma-Aldrich. Graphene was acquired from Graphene Supermarket (New York, USA). All reagents used in this work were of analytical grade and all aqueous solutions were prepared with ultrapure water with resistivity not less than 18 MΩ cm obtained from a Milli-Q Direct-0.3 (Millipore) purification system.

A stock solution of 1.0×10^{-3} mol L^{-1} ofloxacin was prepared by dissolving 3.6 mg of the compound in 10.0 mL of supporting electrolyte solution prepared in ultrapure water. The mixture was sonicated for 2 min to ensure the complete dissolution of ofloxacin.

2.2. Apparatus

Electrochemical experiments were performed using a model PGSTAT-30 potentiostat/galvanostat (Metrohm-Autolab, Utrecht, Netherlands) fitted with an electrochemical cell containing three electrodes: Ag/AgCl (3.0 mol L^{-1} KCl) reference electrode (Analion), a platinum wire as the counter electrode and a modified carbon paste electrode (CPE) as the working electrode (2.5 mm diameter). The apparatus was controlled by the GPES 4.9 software (Eco Chemie).

The pH measurements were performed using an Orion Expandable Ion Analyzer (model EA-940, USA) employing a combined glass electrode with an Ag/AgCl (3.0 mol L^{-1} KCl) external reference electrode.

The morphologic features of the graphene oxide were evaluated using images acquired by field-emission gun scanning electron microscopy (FEG/SEM, Supra 35-VP, Carl Zeiss, Germany) with an electron beam energy of 25 keV and by transmission electron microcopy (TEM, FEI Tecnai G2F20) 200 kV.

A Shimadzu UV-2550 UV/Vis spectrometer with a quartz cuvette (optical path length of 1 cm) was employed for analytical determination of ofloxacin by the comparative method [35].

2.3. Synthesis of GO

Graphene oxide (GO) was obtained by functionalization of graphene using an acid treatment procedure as reported previously [38]. Initially, 100 mg of graphene was treated with a total of 120 mL of conc. H_2SO_4/conc. HNO_3 in the following volumetric ratios: 1:1, 1:3, and 3:1 (v/v). This mixture was stirred for 12 h and the obtained suspension was washed with deionized water until pH 6.5–7.0. Then, the suspension was dried at 100 °C for 12 h. The obtained electrodes were tested using a 2.44×10^{-3} mol L^{-1} $[Fe(CN)6]^{3-}$ in 0.1 mol L^{-1} KCl solution and, the higher magnitude of analytical signal was achieved for 1:1 (v/v) acids ratio (not shown).

2.4. Preparation of the modified carbon paste electrode

The modified carbon paste electrode was prepared using a mixture of 94 mg of graphite powder, 5.0 mg of GO and 1.0 mg of ionic liquid (1-buthyl-3-methylimidazolium tetrafluoroborate). The mixture of these materials was carefully homogenized for 30 min using a mortar and pestle. Afterwards, 80 μL (65 mg) of mineral oil was added to obtain a paste. The prepared paste was then packed into the cavity of the Teflon working electrode (2.5 mm i.d., 1 mm depth), where a Pt disk was used to provide the electrical contact. The obtained modified electrode was named as GO-IL/CPE. Partially modified CPEs were prepared for the comparative studies. Thus, an IL/CPE was made using 1.0 mg of ionic liquid and 99 mg of graphite and a bare CPE was made using 100 mg of graphite. The same amount of mineral oil (Nujol) was used for preparation of the partially modified CPEs.

2.5. Preparation of samples

The voltammetric procedure developed using the GO-IL/CPE as an electrochemical sensor was evaluated in the ofloxacin determination in different matrice samples. The analyzed samples were commercial ophthalmic formulations and biological urine samples. In the following sections, the preparation procedures adopted for these samples are described in detail.

2.5.1. Preparation of ophthalmic samples

Two commercial ophthalmic formulation samples containing ofloxacin at a concentration of 3 mg mL^{-1} were purchased in local drugstores and subjected to a simple sample preparation procedure: 12 μL of each ophthalmic sample was diluted in 10 mL of ultrapure water (dilution of 830 times) resulting in sample stock solution containing ofloxacin at 1.0×10^{-5} mol L^{-1}. Next, an adequate volume of this stock solution was added in the electrochemical cell containing 10 mL of supporting electrolyte solution and the voltammetric measurement collect.

2.5.2. Preparation of biological urine samples

The biological urine sample was collected from one healthy individual. The urine sample was spiked with two different concentration levels of ofloxacin (5.0×10^{-8} and 1.0×10^{-7} mol L^{-1}) and analyzed using the voltammetric procedure. For this, an adequate volume of the urine sample stock solution (1.0×10^{-5} mol L^{-1}) was added in the electrochemical cell containing 10 mL of supporting electrolyte solution and the voltammetric measurement collect.