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Polyfurfural film modified glassy carbon electrode for highly sensitive nifedipine determination

Qiang Zeng, Tianyan Wei, Min Wang, Xinjian Huang, Yishan Fang, Lishi Wang*

Key Laboratory of Fuel Cell Technology of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China

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ABSTRACT

A sensitive and convenient electrochemical strategy is developed for the determination of nifedipine basing on a polyfurfural film modified glassy carbon electrode (GCE) by the one-step electropolymerization of furfural. The prepared polyfurfural film/GCE exhibits excellent electrocatalytic activity towards nifedipine. A series of experimental parameters including the pH of supporting electrolyte, accumulation time and potential for nifedipine is also considered and optimized. Under optimal conditions, the proposed nifedipine sensor has a wide linear detection range from 1×10^{-8} to 7×10^{-6} mol dm^{-3}, with a low detection limit of 5×10^{-9} mol dm^{-3}. The proposed nifedipine sensor also displays excellent selectivity, stability and reproducibility. In particular, it shows splendid analytical performance for the determination of nifedipine in real pharmaceutical and human urine samples in practice.

1. Introduction

As an efficient calcium channel blocker, 1,4-dihydro-2,6-dimethyl-4-(2-nitrophenyl)-3,5-pyridine-dicarboxylic acid dimethyl ester known as nifedipine (Chart 1) has been extensively applied to the treatment of angina pectoris, arterial hypertension and various cardiovascular diseases [1,2]. However, many undesired side effects, such as nausea, vomiting, dizziness, pounding heartbeats are caused by the overdose of nifedipine in use [3,4]. Thus, a reliable and sensitive method is highly necessary and important for the detection of nifedipine in practice. Various chromatographic and spectroscopic methods have been previously reported for the quantitative determination of nifedipine, such as high performance liquid chromatography (LC) in conjunction with a UV detector [5,6], gas chromatography (GC) coupled to an electron capture detector [7,8], the combination of gas chromatography and mass spectrophotometry (GC-MS) [9], multivariate image analysis-thin layer chromatography [10], LC–MS/MS [11], spectrophotometric detection [12], and fluorometry [13]. However, the main disadvantage of these methods is their time-consuming and complicated experimental processes.

Comparing to the conventionally chromatographic and spectroscopic methods, electrochemical monitoring becomes an attractive alternative for the determination of nifedipine because of its rapid response, simplicity of operation as well as the minimal sample pretreatment involved [14–16]. In particular, nifedipine is well known as an electroactive compound, having two redox centers [2,17,18], i.e., the nitroaromatic and dihydropyridine (DHP) groups where the former is electrochemically reducible and the latter is electrooxidizable. Based on these specific electrochemical properties, significant research effort has been made in developing electrochemical nifedipine sensors by various electrode materials, such as β-cyclodextrin incorporated multi-walled carbon nanotubes [17], activated glassy carbon electrode (activated GCE) [2], Ag nanoparticles modified glassy carbon electrode (Ag nanoparticles/GCE) [19] and modified carbon paste electrode (CPE) [20] or a boron-doped diamond electrode for the quantification of nifedipine-like substances e.g., amlodipine [21]. For the determination of nifedipine, these materials did their jobs, however, the resulted sensors lack satisfied sensitivity. On the other hand, polymer-modified electrodes have been also put in the spotlights of sensing applications with superiorities of good stability, containing multiple active sites, homogeneity in electrochemical deposition and strong adherence to electrode surface [22–26]. The strategy of electropolymerization provides advantages to immobilize polymers (e.g., poly-aniline film [27], poly-o-phenylenediamine film [28], poly (naphthol green B) film [29]) onto an electrode surface, giving controllable film thickness, permeation and charge

* Corresponding author at: Room 222, 15th Building, South China University of Technology, 510640. Fax: +86 20 87112906.
E-mail address: wanglsh@scut.edu.cn (L. Wang).

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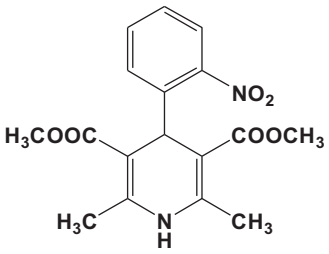

Chart 1. Chemical structure of nifedipine.

transport characteristics by easily adjusting the electrochemical parameters [30]. In particular, the polyfurfural film on different electrodes such as Pt electrode [31,32], low carbon steel [33] and GCE [34] shows good adherence and electrical conductivity, avoiding a complicated electrode preparation process. Moreover, the polyfurfural film modified GCE also exhibits excellent electrocatalytic activity to the oxidation of hydroxy and the reduction of nitro reported by our research group recently [34,35] due to the promoted electron transfer by the conjugated π-electron backbones of polyfurfural [32,34].

In this contribution, a polyfurfural film modified GCE has been fabricated to study the electrochemical behavior of nifedipine by a convenient one-step electropolymerization method. In particular, the polyfurfural film/GCE shows admirable electrocatalytic activity towards nifedipine. Effects of different parameters on the ability of this modified electrode toward the reduction process of nifedipine have been also investigated. Under optimum conditions, differential pulse adsorptive striping voltammetry (DPAdSV) is applied to the direct determination of nifedipine, achieving a significantly wide linear range from 1×10^{-8} to 7×10^{-6} mol dm^{-3} with a detection limit of 5×10^{-9} mol dm^{-3}. The proposed sensor is highly sensitive, stable and reproducible and successfully used in the quantitative determination of nifedipine in real pharmaceutical and human urine samples. To best of our knowledge, it is the first report of the electrochemical determination of nifedipine by using the polyfurfural film/GCE. This developed method would have a tremendous meaning to pharmaceutical and biological samples analysis.

2. Experimental

2.1. Reagents and solutions

Nifedipine (analytical grade) and Furfural (GC, 98%) were acquired from Aladdin Chemical Reagent Co. Ltd. (Shanghai, China). Sodium perchlorate was obtained from Fuchen Chemical Reagent Company (Tianjin, China). All other chemicals were of analytical reagents grade and used without further purification. Britton-Robinson (BR) buffers solution of pH 3-11 (mixtures of 0.04 mol dm^{-3} of acetic, 0.04 mol dm^{-3} of orthophosphoric, and 0.04 mol dm^{-3} of boric acids; adjusted to the required pH with 0.2 mol dm^{-3} of sodium hydroxide solution) was prepared. Stock solution of nifedipine was prepared as 0.001 mol dm^{-3} in methanol and diluted to different concentrations before use by mixing with BR (pH 9.0). The stock solution should be stored in the dark under refrigeration to avoid decomposition and it showed excellent stability under these conditions for at least 30 days. All aqueous solutions were prepared using double-distilled water.

To prepare real pharmaceutical samples, two tablets of nifedipine (labeled 10.0 mg, Sinopharm Group Co. Ltd, Guangzhou, China) were weighed and grounded to a homogeneous fine powder by using a mortar with pestle and then the obtained powder was dissolved in 10 mL methanol by ultrasonication. The adequate amount (1 mL) of prepared solution with particular amount of nifedipine (giving finally added concentrations as 1.0, 2.0, 3.0 and 4.0 μmol dm^{-3}, respectively) was diluted to 100 mL by the Britton-Robinson (BR, pH 9.0) buffer solution. Finally, the resulted solution was transferred to electrochemical cell for the voltammetric determinations.

Human urine samples were collected from four healthy volunteers who did not undergo any treatments by pharmaceuticals containing nifedipine. Each sample (5 mL) was centrifuged for 10 min at 12,000 rpm to separate the aqueous and organic layers and the supernatant was filtered using a 0.45 μm filter. The filtrate was diluted by BR buffer solution (pH 9.0) in a 1:3 (urine:buffer) volume ratio to 20 ml. By standard addition method, extra nifedipine was added to these samples for further analysis, making the added concentration of nifedipine as 0.05, 0.1, 0.2 and 0.3 μmol dm^{-3}, respectively.

2.2. Fabrication of polyfurfural film modified glassy carbon electrode

A 3 mm diameter bare GCE (Xianren, Shanghai, China) was sequentially polished with 0.3 and 0.05 μm alumina powder to obtain a mirror-like surface prior to use, then washed ultrasonically in anhydrous ethanol and doubly distilled water for 5 min, respectively. The cleaned GCE was dried with nitrogen stream for further modification. The electropolymerization of furfural was performed in acetonitrile containing furfural (0.01 mol dm^{-3}) and sodium perchlorate (0.06 mol dm^{-3}) by cyclic voltammetry between −0.8 V and +2.8 V at a scan rate of 100 mV s^{-1} for 5 cycles. After electropolymerization, the polyfurfural film modified electrode was washed with doubly distilled water to remove all chemicals which were physically absorbed.

2.3. Apparatus and method

Electrochemical measurements were performed on a CHI660E electrochemical workstation (Chenhua, Shanghai, China) with a conventional three-electrode cell. In the process of electropolymerization, a three-electrode configuration consisting of a bare GCE as the working electrode, a Ag/AgCl (0.01 mol dm^{-3} of $NaClO_4$ in acetonitrile) electrode as the reference electrode and a platinum wire as the counter electrode was used. While in the process of determination, the polyfurfural film/GCE working electrode and the saturated calomel reference electrode (SCE) were utilized instead. Electrochemical impedance spectroscopy (EIS) was obtained with a wide frequency range from 0.1 Hz to 10 kHz in 0.1 mol dm^{-3} of KCl solution containing 5 mmol dm^{-3} of $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ with a sine wave of 5 mV amplitude. The surface morphology was characterized using a field emission scanning electron microscope (FE-SEM; Zeiss Ultra55, Germany).

Before each measurement, the accumulation procedures of working solution at the working electrode were carried out at open-circuit for 75 s while the solution was stirred at 400 rpm with a magnetic stirrer. DPAdSV and CV signals were recorded in BR buffer solution (pH 9.0) containing different concentration of nifedipine. For DPAdSV, the parameters such as amplitude (0.05 V), pulse width (0.05 s) and pulse period (0.5 s) have been optimized and used in all measurements.

For the determination of nifedipine, the detection limit, C_m, was obtained using equation *Eq.* (1):

$$C_m = 3S_b/m \quad (1)$$

where m is the slope of the calibration plot (1.489 μA μmol dm^{-3}) in the linear range (0.01 to 7 μmol dm^{-3}), and S_b is the standard deviation of the blank response which is obtained from 20 replicate measurements of the blank BR buffer solution.