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A dysprosium nanowire modified carbon paste electrode for determination of levodopa using fast Fourier transformation square-wave voltammetry method

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ABSTRACT

A new detection technique called the fast Fourier transform square-wave voltammetry (FFT-SWV) is based on the measurements of electrode admittance as a function of potential. The response of the detector (microelectrode) is fast, which makes the method suitable for most applications involving flowing electrolytes. The carbon paste electrode was modified by nanostructures to improve better sensitivity. The response is generated by a redox processes. The redox property of L-dopa was used for determination of it in human serum and urine samples. The support electrolyte that provided a more defined and intense peak current for L-dopa determination was at 0.05 mol l^{-1} acetate buffer pH 7.0. Synthesized dysprosium nanowires make more effective surface like nanotubes [P.M. Ajayan, S. Iijima, Nature 361 (1993) 333; I.A. Merkoc, Microchim. Acta 152 (2006) 157; F.H. Wu, G.C. Zhao, X.W. Wei, Z.S. Yang, Microchim. Acta 144 (2004) 243; L. Liu, J. Song, Anal. Biochem. 354 (2006) 22] so they are good candidates for using as a modifier for electrochemical reactions. The drug presented one irreversible oxidation peaks at 360 mV versus Ag/AgCl by modified nanowire carbon paste electrode which produced high current and reduced the oxidation potential about 80 mV.

Furthermore, signal-to-noise ratio has significantly increased by application of discrete fast Fourier transform (FFT) method, background subtraction and two-dimensional integration of the electrode response over a selected potential range and time window. To obtain the much sensitivity the effective parameters such as frequency, amplitude and pH was optimized. As a result, C_{DL} of 4.0×10^{-9} M and an LOQ of 7.0×10^{-9} M were found for determination for L-dopa. A good recovery was obtained for assay spiked urine samples and a good quantification of L-dopa was achieved in a commercial formulation.

1. Introduction

The unusual amino acid levodopa (3,4-dihydroxyphenylalanine, L-DOPA) is the precursor required by the brain to produce dopamine, a neurotransmitter (chemical messenger in the nervous system). People with Parkinson's disease have depleted levels of dopamine and levodopa is used to increase dopamine in the brain, which reduces the symptoms of Parkinson's disease. Nevertheless, auto-oxidation of levodopa generates toxic metabolites, such as free radicals, semi-quinones and quinones. In vitro, levodopa is a powerful toxin that is lethal to the culture of neurons, and a few animal studies have shown that chronic levodopa may be toxic in vivo, too [5].

A variety of analytical methods have been developed in order to measure levodopa levels in different sample matrices, such as HPLC [6,7], spectrofluorimetry [8], circular dichroism [9], flow injection analysis [10], spectrophotometric [11,12], photokinetic [13], and catalytic anodic stripping voltammetric [14] methods, etc. Botanists quantitatively estimated the concentration of levodopa in vegetal samples even by measuring the UV absorption at 283 nm after correction for background absorption yet [15,16].

The method which introduced in this paper is very sensitive, inexpensive and fast for detection of L-dopa. The square-wave voltammetry (SWV) has recently been shown to be advantageous for environmental detection of several compounds [17]. The adaptation of this technology to SWV of L-dopa on a (dysprosium nanowire carbone paste electrode) DyN/WCPE could provide a substantial improvement for rapid and very sensitive analysis [18,19].

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Carbon paste electrodes (CPEs), due to their ease of construction, renewability, and compatibility with various types of modifiers, have been widely used as a suitable matrix for preparation of modified electrodes. Further, they show rather low background current compared to the solid graphite or noble metal electrodes [20]. In recent years, application of the CNT-modified carbon paste electrodes showed considerable improvements in electrochemical behavior of biologically important compounds [21,22]. Metal nanowires such as Dysprosium showed behavior like CNTs. A CPE containing 10% (w/w) of DyNW, in comparison with CPE without nanowire, showed a very effective catalytic activity in the electrochemical oxidation of levodopa.

Using the fast Fourier transform method was found very sensitive system in combination by electrochemical method for trace detection of several compounds [23–40]. This paper describes a fundamentally different approach to SWV measurement, in which the detection limits are improved, while preserving the information content of the SW voltammogram. The approach is designed to separate the voltammetric signal and background signal in frequency domain by using discrete fast Fourier transformation (FFT) method. SWV measures the current response while rapid alternating potentials are applied during a staircase scan, whereas CV, which uses only a forward and reverse linear dc scan, is not sensitive to the potential dependence of changes that occur in the double layer.

However, the reported methods suffer from limitations such as material waste and time consumption, because a number of preliminary steps are often required to obtain the species from the sample matrix. In this paper a very simple and sensitive electrochemical method was introduced for determination of levodopa.

2. Experimental

2.1. Instrumentation

The electrochemical instrument, ultra voltammetry, a home made potentiostate were used for the present voltammetric measurements. All electrochemical experiments were done using a setup comprised of a PC PIV equipped with a data acquisition board (PCL-818H, Advantech Co.) was used to output an analog waveform to the working electrode and acquire current readings from the working electrode that connected to a custom made potentiostate. The card and accompanying dynamic link libraries allowed waveform generation and current sampling to be synchronized, which was essential in interpreting SWV current response. The memory and CPU requirements of the computer were dictated by the nature of the data acquisition requirements. Software was developed using Delphi 6.0 to repeatedly apply a waveform to the working electrode and synchronously acquire, analyze, and store the current data. The data could be interpreted in real time, or stored data could be loaded and reanalyzed to generate electropherograms. The algorithms used to interpret the current response from each waveform cycle were discussed before by [41]. Most of the waveform parameters could be modified from within the software; including the pre- and post-scan potential/time, square-wave frequency/amplitude, dc ramp initial/final potential, and ramp time.

2.2. Carbon paste electrode

The nanowires was synthesized based on the procedure which describe by Li and coworkers [42,43], the TEM image of Dysprosium nanowire was presented in Fig. 1. The dysprosium Nanowire Carbone paste electrode (DyNW/CPE) was prepared by hand-mixing 0.97 g graphite powder, 0.03 g DyNW, and 0.34 ml paraffin oil adequately in a gate mortar. A portion of the resulting paste was then packed firmly into the electrode cavity (1.0 mm diameter) of a polytetrafluorethylene (PTFE) sleeve. The unmodified CPE was prepared in a similar way using 1.25 g graphite powder and 0.45 ml paraffin oil. Electrical contact was established via a copper wire. The surfaces of all the modified and unmodified CPEs were carefully smoothed on weighing paper and rinsed with twice distilled water prior to each measurement.

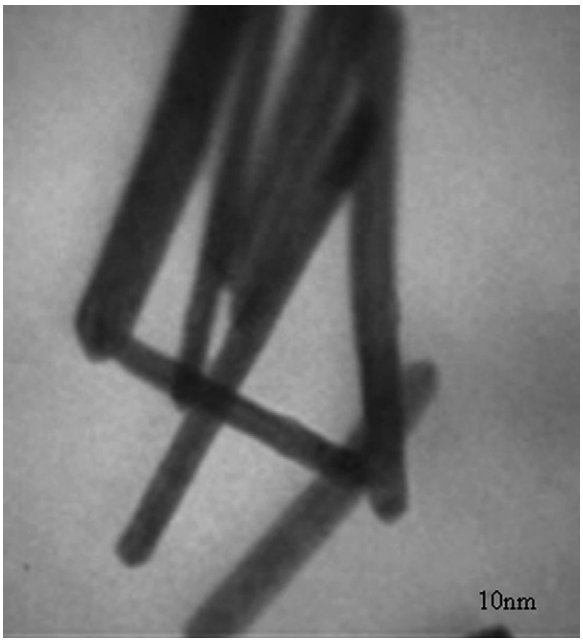

Fig. 1. The TEM image of Dysprosium nanowire.

2.3. Materials and reagents

All chemicals and reagents were of analytical grade quality. L-dopa was a gift from Drug and Food quality control, Tehran, Iran. A stock solution of 1.0×10^{-5} M of L-dopa was prepared in doubly distilled water at 4 °C. More dilute solutions were prepared daily with deionized water just before use. The phosphate buffer (pH 3–9), Britton-Robinson (0.04 M of Phosphoric acid, acetic acid and boric acid) and acetate buffer were prepared using analytical grade reagents and were used as supporting electrolytes. All the solution was made by double distilled water.

2.4. Stripping voltammetry

In this new method to improve the detector sensitivity, the FFT-SWV technique was modified in the potential excitation waveform and current sampling and data processing Fig. 2. The potential waveform consisted of three sections; (a) electrode conditioning and (b) accumulation part (c) measurement the potential waveform contained three additional potential steps, E_{c1} to E_{c2} (for cleaning the electrode surface) and Es (for accumulation of L-dopa). As is shown in Fig. 2, the measurement part of the waveform contains multiple SW pulses with amplitude of E_{sw} and frequency of f_o, were superimposed on a staircase potential function, which was changed by a small potential step of ΔE. The values of potential pulse of SW (E_{sw}) and ΔE were in a range of few mV (10–50 mV). In potential ramp, the currents sampled four times per each SW polarization cycle. After preparing the solution, the measurements were carried out in the continuous fast Fourier transform stripping square-wave voltammetric mode (FFT-SW). A typical experiment consisted of three consecutive steps with the following experimental condi-