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Coulometric differential FFT admittance voltammetry determination of Amlodipine in pharmaceutical formulation by nano-composite electrode

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ABSTRACT

An electrochemical detection technique based on combination of was coulometric differential fast Fourier transformation admittance voltammetry (CDFFTAV) and nano-composite film modified glassy carbon electrode was successfully applied for sensitive determination of Amlodipine. The nano-composite film was made by a mixture of ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$), multiwall carbon nanotube and Au nanoparticles as electrochemical mediators. Studies reveal that the irreversible oxidation of Amlodipine was highly facile on the electrode surface. The electrochemical response was established on calculation of the charge under the admittance peak, which was obtained by discrete integration of the admittance response in a selected potential range, obtained in a flow injection analysis. Once established the best operative optimum conditions, the resulting nano-composite film electrode showed a catalytic effect on the oxidation of the analyte. The response is linear in the Amlodipine concentration range of 1.0×10^{-9} to 2.0×10^{-7} M with a detection limit of 1.25×10^{-10} M. Moreover, the proposed technique exhibited high sensitivity, fast response time (less than 6 s) and long-term stability and reproducibility around 96%, and it was successfully used to the determination of Amlodipine content in the pharmaceutical formulation.

1. Introduction

Amlodipine (*S*-2[(2-aminoethoxy) methyl]-4-(2-chlorophenyl)-3-ethoxycarbonyl-5-methoxycarbonyl-6-methyl-1,4-dihydropyridine) (Fig. 1), is a potent calcium channel blocker used for the treatment of hypertension and angina [1]. It is a third-generation dihydropyridine calcium antagonist which is used alone or in combination with other medications for treating high blood pressure, certain types of vasospastic angina, cardiac arrhythmias, coronary heart failure, and hypertension [2–4].

Various methods including high-performance liquid chromatography (HPLC) with amperometric detection [5], HPLC with UV detection [6], HPLC with fluorescence detection [7], liquid chromatography mass spectrometry (LC/MS) [8], capillary gas chromatography (GC) with electron capture detection [9], GC with electron-impact mass spectrometry (EI-MS) [10] and offline solid-phase extraction (SPE) [11] have been used for the determination of Amlodipine.

Recently, nanostructures play interesting rules in various fields of analytical chemistry [12–14]. Multiwall carbon nanotube (MWCNT) has attracted extensive attention for their high electrical conductivity, good chemical stability, and extreme mechanical strength [15–18]. The improvement of electrocatalytic activity of redox couples at carbon nanotube-based electrodes can be attributed to the presence of edge-plane like sites located at the end and in the defect areas. In fact, the insolubility of carbon nanotubes in many solvents hinders the fabrication of carbon nanotubes modified electrodes. The unique properties of gold nanoparticles (AuNPs) such as providing a suitable microenvironment for enzymes to immobilize but keep their biological activity, and facilitating electron transfer between the species and electrode

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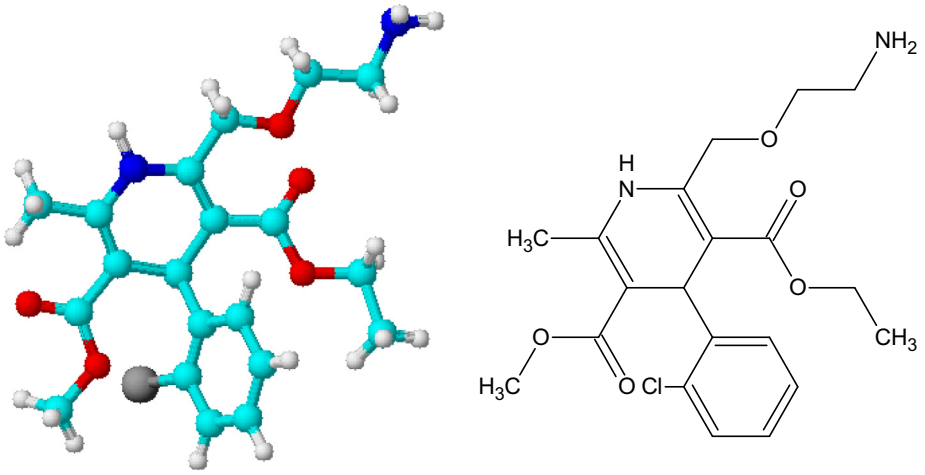

Fig. 1. Chemical 2D and 3D structures of Amlodipine.

surfaces, have led to a wide use of this nanomaterial in construction of electrochemical sensors [19–22]. Moreover, AuNPs play a crucial role in the electrode transduction enhancement of the affinity reaction as well as in the efficiency of MWCNT immobilization in a stable form.

The detection method, fast Fourier transform square wave voltammetry (FFTSWV), which is introduced here, is very sensitive, inexpensive and fast. The square wave voltammetry (SWV) has recently been shown to be advantageous for environmental detection of several compounds [23–27]. 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. In fact, the analyte signal is calculated based on admittance changes related to the changes in electrical double layer.

Using fast Fourier transform (FFT) method was found very sensitive system in combination by electrochemical method for trace detection of compounds [28–39]. In particular, when the magnitude of current is in the range of nano and pico ampere, electrochemical response suffers from existence of environmental noises. This separation allows, digitally filtrating some of the noises and decreasing the bandwidth of the measurement. Further improvement in the signal was gained by two-dimensional integration of the electrode response over a selected potential range and time window of the signal.

In the present paper, a new composite film was prepared by using Au NPs and MWCNT and 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$) as binder and modifier. Where, the electrode response was obtained by a special square wave electrochemical method called coulometric differential FFT admittance voltammetry (CDFFTAV), in flow injection system. For determination of Amlodipine, at first, the admittance of the electrode was measured during the potential ramp and then, the response of the electrode was calculated in form of coulomb.

2. Materials and methods

2.1. Reagents

Amlodipine was purchased from Sigma. The multiwall carbon nanotubes (MWCNTs) with 10–40 nm diameters, 1–25 μm length, SBET: 40–600 m^2/g, with 95% purity were purchased from a local company (Iran). Phosphate buffer solutions (PBS, 0.1 M) with various pH values were prepared by mixing stock standard solutions of K_2HPO_4 and KH_2PO_4 and adjusting the pH with H_3PO_4 or NaOH. The room temperature IL, 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$) was purchased from Aladdin-Reagent Company (China). All other chemicals were of analytical grade and were used without further purification. All solutions were made up with doubly distilled water. The solution of 2 mM $Fe(CN)_6^{4-}$/ $^{3-}$ in 0.02 M PBS was prepared. All other chemicals and solvents used were of analytical grade and used as received without further purification. Double distilled water was used throughout the experiments.

2.2. The electrode preparation

A glassy carbon electrode, GCE (3 mm in diameter) were polished well with 1.0, 0.3 and 0.05 μm alumina slurry and then it was washed thoroughly with doubly distilled water. The electrodes were successively sonicated in 1:1 nitric acid, acetone and doubly distilled water, and then allowed to dry at room temperature.

0.1–0.8 mg of MWCNTs and $EMIMBF_4$ (20 μl) were dispersed in 2 ml *N*,*N*-dimethylformamide (DMF) with the aid of ultrasonic agitation to achieve a well-dispersed suspension. Then, 5 μl of the suspension was dropped on a cleaned GC electrode and let the solvent was evaporated in air. Hence, a uniform film of MWCNTs coats the surface of GC electrode. The electrochemical deposition of Au NPs was performed in 0.2 M Na_2SO_4 aqueous solution of $HAuCl_4$ (1.0 mM). The deposition time was about 20–110 s and the potential was −0.2 V. After that, the surface of the modified electrode was carefully washed with distilled water and dried at room temperature. Finally, the modified electrode was activated by several successive potential scans from 0.4 to 1.0 V with a scan rate of 50 mV/s in phosphate buffer solution (pH 6.0) until a steady voltammogram was obtained. The mean size of the prepared Au NPs was about 30–90 nm, estimated by transmission electron microscopy. The schematic diagram of construction steps and of the view of modified electrode was shown in Fig. 2A. The flow injection analysis, used for measurements, has an eight roller peristaltic pump, a four way injection valve (UltrateckLabs Co., Iran) with 300 μl sample injection loop and four ways cell. The cell was a three-electrode configuration was employed in all experiments, with potentials referring to an Ag/AgCl reference electrode and an auxiliary electrode (2.0 mm in diameter) in the flow cell. Fig. 2B and C shows the diagram of the flow injection analysis system and the electrochemical cell.