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Original Research Article

Electrochemical Amplified Sensor with Mgo Nanoparticle and Ionic Liquid: A Powerful Strategy for Methyldopa Analysis

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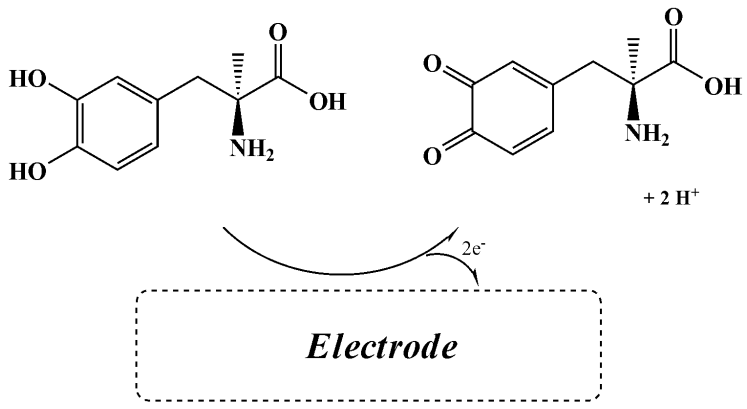
ABSTRACT

In this research, an amplified sensor based on paste electrode (PE) modified with MgO nanoparticle (MgO/NPs) and 1-hexyl-3-methylimidazolium hexafluorophosphate (HMH) was designed and used for determination of methyldopa (MD). The CP/MgO/NPs/HMH showed good catalytic activity toward oxidation of MD and improved drug current about 3.58 times. In addition, CP/MgO/NPs/HMH showed a diffusion process and pH dependence behavior for electro-oxidation of MD in aqueous solution. However, differential pulse voltammogram of CP/MgO/NPs/HMH showed a linear dynamic range to sensing of MD in concentration range 1.0 nM – 400 µM with detection limit 0.5 nM. The recovery range 98.25% - 102.5% was obtained for sensing of MD in real samples using CP/MgO/NPs/HMH.

GRAPHICAL ABSTRACT



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Introduction

Measuring the dose of drugs and determining their concentration in biological samples is a very important way to evaluate the quality and effectiveness of drugs [1-5]. For a long time, various analytical methods have been used as an important strategy to evaluate dose drugs in drug companies [6-8]. In recent years, the data obtained from the measurement of drug compounds have been used as a useful solution to investigate the effect of drug compounds on patients [9-15]. Chromatographic and spectroscopic methods are among the methods used to determine the concentration of drugs in biological media that have been used for years [16-18]. However, the pitfalls of these methods, such as the high cost and in some cases the specificity of the method, have made scholars in this field to devise an alternative solution [19]. Electrochemical methods with high speed and sensitivity of analysis and with the ability to measure in different environments and high selectivity have been introduced today as an alternative method for the analysis of pharmaceutical and biological compounds [20-23]. On the other hand, electrochemical methods can be modified to improve selectivity and sensitivity and can be used for a wide range of compounds [24-27]. Also, with the advent of nanotechnology and the unique properties of nanomaterials in improving the electrical conductivity, a great revolution has taken place in the construction of various electrochemical sensors [28-32]. Today, many reports have been published on the manufacture of electrochemical sensors modified with nanomaterials with unique advantages[33-36].

Many branches of science have used nanomaterials with their attractive and incredible properties in recent years [37-39]. Among these, metal and carbon based nanomaterials are more important than other compounds and have a wide range of applications [40-46]. MgO nanoparticle is a metal oxide based nanomaterials with unique properties and it is a suitable choice for using as catalyst in electrochemical sensors [47, 48].

In this study, CP/MgO/NPs/HMH was suggested as new electrochemical sensor for sensing and determination of methyldopa in biological samples and results showed powerful ability of this sensor for real sample analysis.

Material and methods

Methyldopa (99%), magnesium nitrate (99%), 1-hexyl-3-methylimidazolium hexafluorophosphate (> 97.0), graphite powder (99.99%), sodium hydroxide (> 97.0) and paraffin oil were purchased from Across and Merck companies. I-V was recorded by a Potentiostat/Galvanostat machine (Ivium-Vertex).

Synthesis of MgO/NPs

50 mL magnesium nitrate (1.0 M) was stirred for 30 min at 30 °C. In the next step, 50 mL sodium hydroxide (2.0 M) was added to the magnesium nitrate solution and stirred continuously for 35 min at 30 °C. The precipitated sample was washed seven-times and dried at 120 °C for 11 h. The white powder was calcinate at 450 °C for 5 h.

Fabrication of CP/MgO/NPs/HMH

For fabrication of CP/MgO/NPs/HMH, 0.6 g MgO/NPs + 0.94 g graphite powder was dispersed into 10 mL diethyl ether. After evaporation of diethyl ether, suitable amount of HMH + paraffin oil was added for converting of powder to paste.

Real sample preparation

Dextrose saline were prepared from local pharmacy and centrifuged at 3000 rpm for 20 min. After filtration, samples was diluted by phosphate buffer solution (pH=7.0). The diluted samples was used for real sample analysis by standard addition method.

Result and Dissection

Electrochemical behavior of Methyldopa

Differential pulse voltammograms of methyldopa in the pH range 5.0 – 9.0 was recorded at surface of CP/MgO/NPs/HMH. The results are presented in Figure 1 inset, confirming negative potential shift with increasing in pH value. The plot of potential vs. pH showed a slope of 54.5 mV/pH for electro-oxidation of MD in this pH range that confirmed equal value of proton and electron in redox reaction mechanism of MD according to scheme 1.

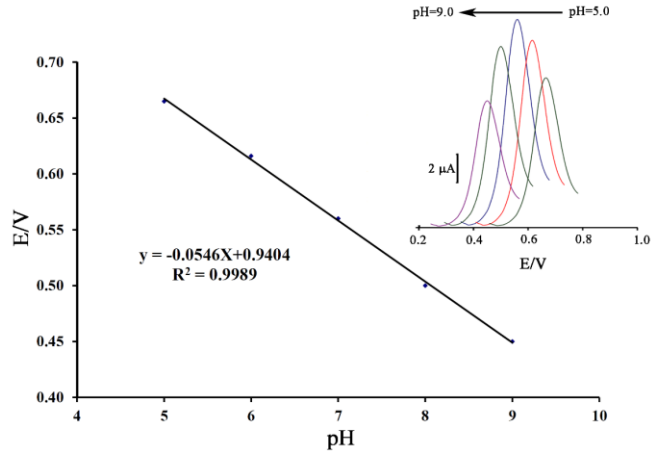
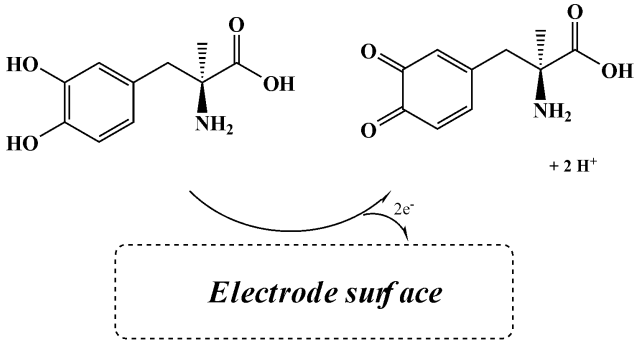


Figure 1: Ep-pH curve for electro-oxidation of 130 µM methyldopa. Inset) Relative DP voltammograms for electro-oxidation of 130 µM methyldopa



Scheme 1. Methyldopa electro-oxidation at electrode surface

On the other hand, oxidation signal of methyldopa in the pH range 5.0–9.0 clearly confirm best electro-oxidation condition at pH=7.0 and this condition was used for next step investigations.

The role of MgO/NPs and HMH as catalysts at surface of paste electrode for sensing of methyldopa was investigated by differential pulse voltammetric method. For this goal, DP voltammogram of 130 µM MD was recorded at surface of CP, CP/MgO/NPs, CP/HMH and CP/MgO/NPs/HMH, respectively (Figure 2, curves a-d). According to the recorded signal, with moving of CP to CP/MgO/NPs/HMH, the oxidation current of methyldopa was improved from 4.06 µA to 14.6 µA that confirm high conductivity of two mediators.

Linear sweep voltammmogram of methyldopa was recorded at surface of CP/MgO/NPs/HMH (Figure 3 inset). Recorded plot showed a linear relation between oxidation signal of methyldopa and $\nu^{1/2}$ with equation I = 0.8653 $\nu^{1/2}$ + 0.5684 (R^2 = 0.9973) that confirm diffusion process [49-51] for redox reaction of drug at the surface of CP/MgO/NPs/HMH.

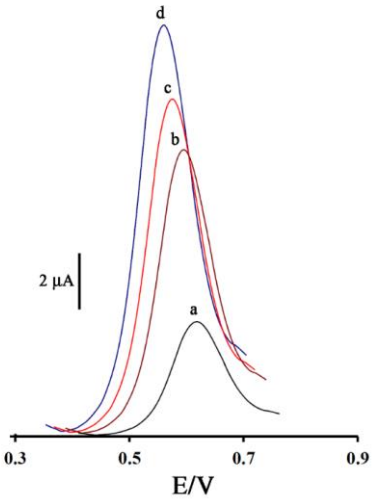


Figure 2: DP voltammogram of 130 µM methyldopa at surface of CP (a), CP/MgO/NPs (b), CP/HMH (c) and CP/MgO/NPs/HMH (d)

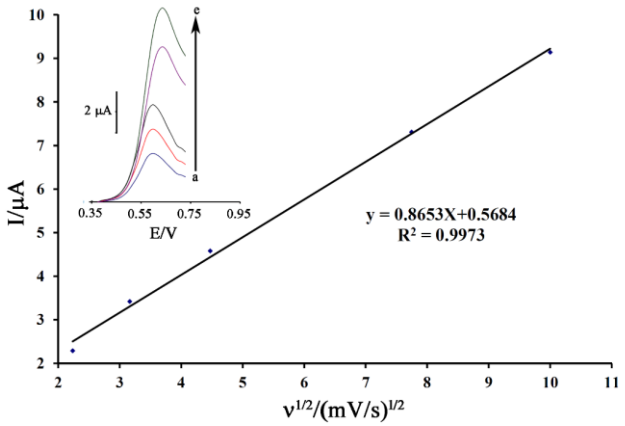


Figure 3: I-$\nu^{1/2}$ curve for electro-oxidation of 500 µM methyldopa. Linear sweep voltammogram of 500 µM methyldopa at scan rate a) 5, b) 10, c) 20, d) 60 and e) 100 mV/s

Linear dynamic range and limit of detection of methyldopa at surface of CP/MgO/NPs/HMH was investigated by DP voltammetric method and results confirmed ability of CP/MgO/NPs/HMH for determination of methyldopa in the concentration range 1.0 nM - 400 µM with detection limit 0.5 nM (Figure 4).

The selectivity of CP/MgO/NPs/HMH as new methyldopa sensor was checked with acceptable error 5% in current and potential in this step. The results showed that CP/MgO/NPs/HMH had good selectivity for determination of 10.0 µM methyldopa in the presence of vitamin C, vitamin B_9, glycine, tryptophan, valine, Na^+, K^+, Cl^-, and Br^-.

In the final step, the CP/MgO/NPs/HMH was used to determine methyldopa in the dextrose saline samples. The results are shown in Table 1 that confirm high ability of CP/MgO/NPs/HMH for determination of methyldopa with recovery range of 98.25% – 102.5% in real samples.

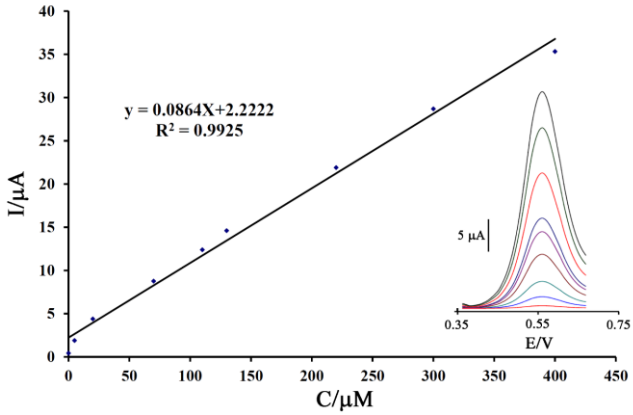


Figure 5: The plot relative to electro-oxidation of methyldopa in concentration range 1.0 nM – 400 µM. DP voltammograms of methyldopa in concentration range 1.0 nM – 400 µM

Table 1: Determination of methyldopa in real sample

Sample	Added (µM)	Expected (µM)	Founded (µM)	Recovery %
dextrose saline	---	---	<LOD	---
	10.00	10.00	10.25±0.65	102.5
	20.00	20.00	19.65±0.87	98.25
Drinking water	---	---	<LOD	---
	5.00	5.00	5.11±0.26	102.2

Conclusion

In this research, due to important determination of methyldopa in biological samples, an amplified sensor was fabricated using catalytic effect of MgO/NPs and 1-hexyl-3-methylimidazolium hexafluorophosphate. The synthesized MgO-NPs showed excellent electro-catalytic activity for sensing of methyldopa in biological media. The CP/MgO/NPs/HMH showed a powerful catalytic activity for determination of methyldopa in the concentration range 1.0 nM - 400 µM with detection limit 0.5 nM in aqueous solution. The recovery range of 98.25% - 102.5% was obtained for sensing of MD in real samples using CP/MgO/NPs/HMH.

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Authors' contributions

All authors contributed toward data analysis, drafting and revising the paper and agreed to be responsible for all the aspects of this work.

Conflict of Interest

We have no conflicts of interest to disclose.

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