Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. *83* (7–8) 863–874 (2018)
JSCS–5118
UDC 547.261.05+546.56'824–31+
544.6.076.32–033.5–032.35:681.586.74
Original scientific paper

Methyldopa electrochemical sensor based on a glassy carbon electrode modified with Cu/TiO_2 nanocomposite

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(Received 30 September 2017, revised 17 January, accepted 29 January 2018)

Abstract: A Cu/TiO_2 nanocomposite modified glassy carbon electrode (Cu/TiO_2/GCE) was fabricated to detect methyldopa by cyclic voltammetry (CV) and different pulse voltammetry (DPV) methods. Compared with bare GCE, the Cu/TiO_2/GCE exhibited excellent electrochemical activity for the oxidation of methyldopa. Using DPV technique, the calibration curves for methyldopa were found linear in the concentration range of 0.5–800.0 μM and the detection limit (S/N = 3) was calculated to be 0.23 μM. Additionally, the prepared electrochemical sensor of Cu/TiO_2/GCE demonstrated a practical feasibility in methyldopa tablets and in urine samples analysis.

Keywords: methyldopa; Cu/TiO_2 nanocomposite; graphite screen printed electrode; voltammetry.

INTRODUCTION

Methyldopa, a catechol derivative, is an old antihypertensive agent that has been used to treat high blood pressure since the 1960s.[1,2] It is a structural analogue of dopa (dihydroxyphenyl alanine), an anti-Parkinsonism medication; in fact it has an amino acid skeleton with a catechol group and a methyl group on the α-carbon of the side chain.[3–6]

Methyldopa operates through the biotransformation to methyl norepinephrine in the adrenergic nerve terminals.[7] Inhibition of the aromatic amino acid decarboxylase (DOPA decarboxylase) may be one of its functions, this enzyme acts in the biosynthetic pathway of catecholamine's,[8] and converts l-DOPA to the dopamine precursor of epinephrine and norepinephrine.[6–9]

The determination of methyldopa for both pharmaceutical and clinical reasons[10,11] can be performed with various analytical techniques like spectro-

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https://doi.org/10.2298/JSC170930024T

photometry,[12,13] gas chromatography,[14] high performance liquid chromatography (HPLC),[15] chemiluminescence,[16] kinetic methods,[17] ^{1}H-NMR[18] and voltammetric determination,[19] that have been explained for the quantification of catecholamine drugs in dosage forms and biological fluids in the literature. Nonetheless, each mentioned method has disadvantages such as selectivity, the use of organic solvents, long analysis time, complex sample preparation procedures, and costs. In between them, the electrochemical methods are simple, rapid and high sensitive, with no need for sample pretreatment.[20]

Several electrochemical techniques in the field of pharmaceutical analysis have been used for the determination of biological compounds[21] and drug compounds[22] including voltammetry, potentiometry, etc. Some advantages like simplicity, sensitivity, reasonable accuracy and precision, high dynamic range, less sensitivity to the matrix effects, lower cost, and rapidity have aroused great interests for the application of these methods.[23] Furthermore, the selectivity and sensitivity of ordinary electrochemical methods can improve for analysis of drugs in complex matrix such as pharmaceutical and biological samples by the modification of the electrode surface. Application of these sensors can be useful for the trace analyzing of the electroactive species and to eliminate overlapping of the signals in simultaneous analysis.[24] Many kinds of surface structures are being prepared and this technique remains a field of high activity.[25-27]

In recent years, the nanostructured materials including metal nanoparticles, metal oxides and carbon nanotubes have been used for the designing of the modified electrodes for the biological, pharmaceutical and environmental purposes.[28,29] Some features like finite small size, high porosity, high specific surface area, and special physical or chemical properties make these material great modifiers in the field of electroanalysis and electrocatalysis.[31] They have similar properties to other kinds of bulk materials, but they offer additional advantages including enhanced electron transfer, fast kinetics of the electrode processes, and large edge plane/basal plane ratios.[32] The shape and the size of the nanostructures determine the conductivity changes of the materials.

Among them, transition metals oxides often have semiconductor properties, such properties can improve by decreasing the size of the crystals. So it is clear that nanoparticles of these oxides exhibit better function. They are used for the construction of the electrodes for biocells, photogalvanic cells, fuel cells and supercapacitors.[33,34] Nano metal hydroxides/oxides have outstanding properties such as high surface area and enhanced chemical/electrochemical activities.[35] In between them, TiO_2 has exceptional properties, such as high conductivity, high inertness, stability, non-toxicity, bio-compatibility, low cost, etc.[36,37] TiO_2 may be used with different shapes such as nanoparticles, nanotubes, and nanoneedles in the electrochemical sensors and biosensors.[38] Unusual properties of nanosized TiO_2 such as large surface area, special electronic properties, and strong absorpt-

ive and catalytic ability make it a benchmark over the other nano oxides.[39] On the other hand, modified electrodes with copper and copper oxide can catalyze the oxidation reaction of biosubstances.[40] Copper nanoparticles are important because of cost-effectiveness and high electrical conductivity.[41]

The present work reports the synthesis and characterization of Cu/TiO_2 nanocomposite, followed by its immobilization on the surface of a glassy carbon electrode to develop a voltammetric sensor reported for the electrocatalytic determination of the methyldopa. To the best of our knowledge, no study has been reported for this sensor before. Eventually, we evaluate the analytical performance of the suggestion sensor for methyldopa determination in real samples.

EXPERIMENTAL

Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands). The experimental conditions were controlled with general purpose electrochemical system (GPES) software. A conventional three electrodes cell was used at 25±1 °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and the Cu/TiO_2/GCE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was employed for pH measurements.

All solutions were freshly prepared with double distilled water. Methyldopa and all other reagents were of analytical grade and were obtained from Merck chemical company (Darmstadt, Germany). The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0–9.0.

Synthesis of Cu–TiO_2 nanocomposite

TiO_2 and Cu doped TiO_2 nanopowder was prepared by the controlled sol-gel method with titanium(IV) *n*-butoxide $Ti(OCH_2CH_2CH_2CH_3)_4$ as raw materials. All the chemicals were purchased from Merck (Darmstadt, Germany) and were used without any further purification. Deionized water obtained with a Milli-Q purification system (Millipore, Bedford, MA, USA), and filtered through 0.45 μm Millipore solvent filter, was used throughout. The dopant starting material was metallic copper sulphate. In a typical process, 5 ml of $Ti(OBu)_4$ was dissolved in 15 ml of absolute ethanol in a dry atmosphere and ultrasonically dispersed to produce a mixture (solution A). Meanwhile, 5mL of water and 1mL of HNO_3 (65%) were added to another 20 mL of absolute ethanol in turn, to form an alchol/acid/water solution (solution B). After the two resulting solutions were stirred, respectively, the solution A was slowly added dropwise to the solution B under vigorously stirring to carry out a hydrolysis. Subsequently, the roughly stirring was conducted so that the temperature was raised from room temperature to 80 °C at the end of the reaction. The gel was dried in the air for about 24 h at 85 °C and subsequently the resulting material was powdered and then calcined in an electric muffle furnace at 450 °C for 2 h to obtain crystalline powders of TiO_2. Cu doped TiO_2 nanoparticles were synthesized using almost the same method. The molar amount of transition metal ion dopant (Cu^{2+}) was calculated in order to substitute 1 % of titanium ions in TiO_2 and was solubilized in an appropriate amount of ethanol/nitric acid/water solution prior to the hydrolysis. The remaining procedures were the same as described above. After hydrolysis, the greenish transparent sol was obtained. A typical SEM image of the synthesized Cu–TiO_2 nanocomposite is shown in Fig. 1.

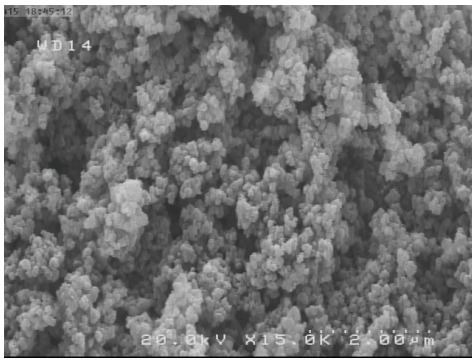

Fig. 1. SEM image of synthesized Cu–TiO_2 nanocomposite.

Preparation of modified electrode

The bare screen-printed electrode was coated with Cu/TiO_2 nanocomposite as follows. A stock solution of Cu/TiO_2 in 1 mL aqueous solution was prepared by dispersing 1 mg Cu/TiO_2 with ultrasonication for 1 h, and a 5 µl aliquot of the Cu/TiO_2/H_2O suspension solution was cast on the carbon working electrodes, and waiting until the solvent was evaporated in room temperature.

Preparation of real samples

Five methyldopa tablets (labelled 250 mg per tablet) were ground. Then, the tablet solution was prepared by dissolving 250 mg of the powder in 25 mL water by ultrasonication. Then, different volumes of the diluted solution were transferred into a 25 mL volumetric flasks and diluted to the mark with phosphate buffer solution (PBS, pH 7.0). The methyldopa content was analyzed by the proposed method using the standard addition method.

Urine samples were stored in a refrigerator immediately after collection. Ten milliliters of the sample was centrifuged for 15 min at 2000 rpm. The supernatant was filtered out using a 0.45 µm filter. Then, different volumes of the solution were transferred into a 25 mL volumetric flasks and diluted to the mark with PBS (pH 7.0).Then the diluted urine samples were spiked with different amounts of methyldopa.

RESULTS AND DISCUSSION

Electrocatalytic oxidation of methyldopa at a Cu/TiO_2/GCE

The electrochemical behaviour of methyldopa is dependent on the pH value of the aqueous solution. Therefore, the pH optimization of the solution seems to be necessary in order to obtain the electrocatalytic oxidation of methyldopa. Thus the electrochemical behaviour of methyldopa was studied in 0.1 M PBS in different pH values ($2.0 < pH < 9.0$) at the surface of Cu/TiO_2/GCE by cyclic voltammetry (CV). It was found that the electrocatalytic oxidation of methyldopa at the surface of Cu/TiO_2/GCE was more favoured under neutral conditions, than in acidic or basic medium. Thus, the pH 7.0 was chosen as the optimum pH for electrocatalysis of methyldopa oxidation at the surface of Cu/TiO_2/GCE.

Fig. 2 depict the CV responses for the electrochemical oxidation of 400.0 µM methyldopa at Cu/TiO_2/GCE (curve a) and bare GCE (curve b). The anodic peak potential for the oxidation of methyldopa at Cu/TiO_2/GCE (curve a) is about

430 mV compared with 540 mV, for that on the bare GCE (curve b). Similarly, when the oxidation of methyldopa at the Cu/TiO_2/GCE (curve a) and bare GCE (curve b) are compared, an extensive enhancement of the anodic peak current at Cu/TiO_2/GCE, relative to the value obtained at the bare GCE (curve b), is observed. In other words, the results clearly indicate that the Cu/TiO_2 nanocomposites improve the methyldopa oxidation signal.

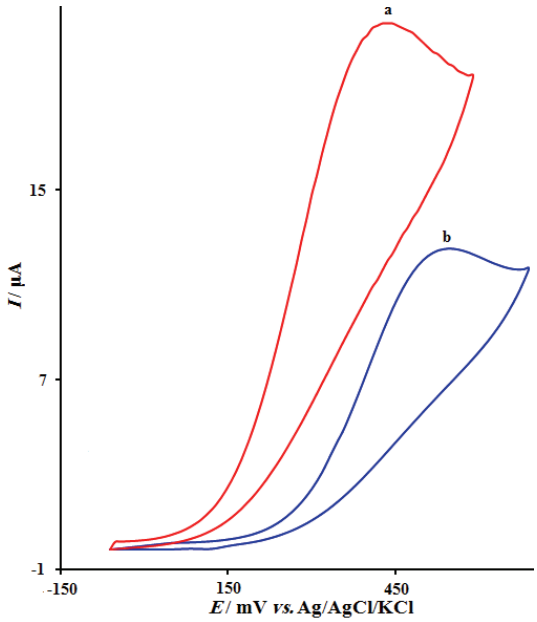

Fig. 2. Cyclic voltammograms of: a) Cu/TiO_2/GCE and b) bare GCE in 0.1 M PBS (pH 7.0) in the presence of 400.0 μM methyldopa at the scan rate 50 mV s^{-1}.

The effect of potential scan rates on the oxidation current of methyldopa has been studied (Fig. 3). The results showed that increasing in the potential scan rate induced a rise of the peak current. In addition, the oxidation process is diffusion controlled, as deduced from the linear dependence of the anodic peak current (I_p) on the square root of the potential scan rate ($v^{1/2}$), over a wide range from 10 to 400 mV s^{-1}.

Fig. 4 shows a Tafel plot that was drawn from points of the Tafel region of the LSV (Linear sweep voltammetry). The Tafel slope of 0.171 V, obtained in this case, agrees well with the involvement of one electron in the rate determining step of the electrode process, assuming a charge transfer coefficient of $\alpha = 0.65$.[42]

Chronoamperometric measurements

Chronoamperometric measurements of methyldopa at Cu/TiO_2/GCE were carried out by setting the working electrode potential at 0.48 $V_{Ag/AgCl/KCl}$ for the various concentration of methyldopa in PBS, pH 7.0 (Fig. 5). For an electroactive material (methyldopa in this case) with a diffusion coefficient of D, the current obs-

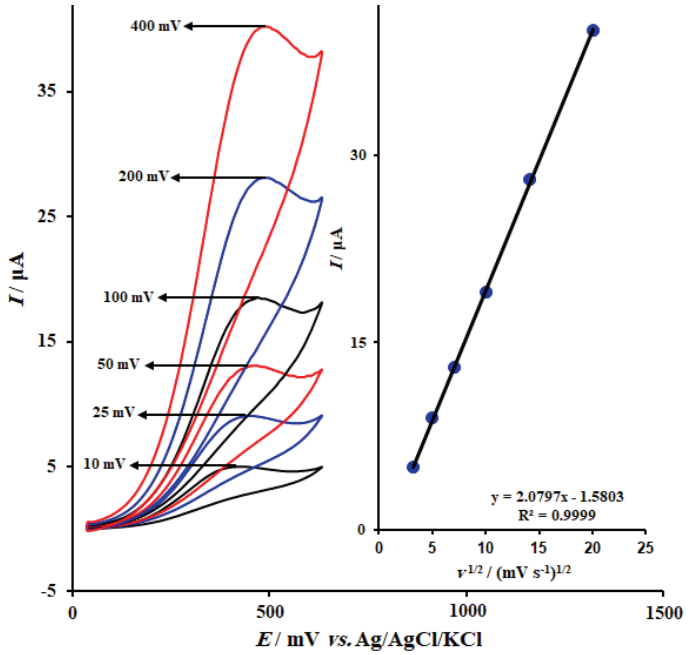

Fig. 3. Cyclic voltammograms of Cu/TiO_2/GCE in 0.1 M PBS (pH 7.0) containing 200.0 µM methyldopa at various scan rates (10, 25, 50, 100, 200 and 400 mV s^{-1}, respectively). Inset: variation of cathodic peak current vs. $v^{1/2}$.

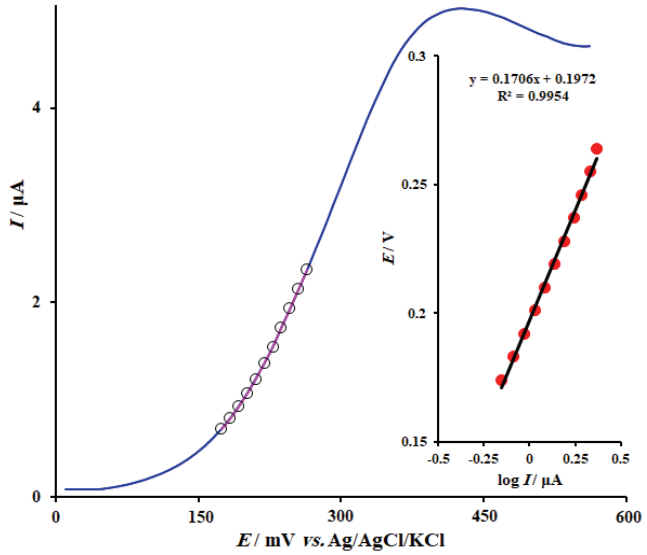

Fig. 4. LSV (at 10 mV s^{-1}) of electrode in 0.1 M PBS (pH 7.0) containing 200.0 µM methyldopa. The points are the data used in the Tafel plot. The inset shows the Tafel plot derived from the LSV.

erved for the electrochemical reaction, at the mass transport limited condition, is described by the Cottrell equation:[42]

$$I = nFAD^{1/2}c_b\pi^{-1/2}t^{-1/2} \quad (1)$$

where D and c_b are the diffusion coefficient ($cm^2\ s^{-1}$) and the bulk concentration (mol cm^{-3}), respectively. Experimental plots of I *vs.* $t^{-1/2}$ were employed, with the best fits for different concentrations of methyldopa (Fig. 5A). The slopes of the resulting straight lines were then plotted vs. methyldopa concentration (Fig. 5B). From the resulting slope and Cottrell equation, the mean value of the D was found to be 4.92×10^{-5} cm^2/s.

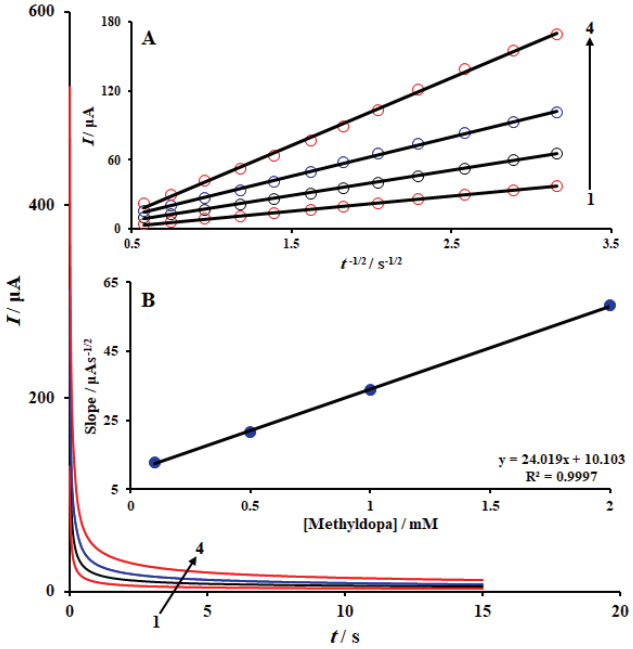

Fig. 5. Chronoamperograms obtained at Cu/TiO_2/GCE in 0.1 M PBS (pH 7.0) for different concentration of methyldopa. The numbers 1–4 correspond to 0.1, 0.5, 1.0 and 2.0 mM of methyldopa. Insets: A) Plots of I *vs.* $t^{-1/2}$ obtained from chronoamperograms 1–4; B) plot of the slope of the straight lines against methyldopa concentration.

Calibration plot and limit of detection

The peak current of methyldopa oxidation at the surface of the modified electrode can be used for the determination of methyldopa in solution. Therefore, the differential pulse voltammetry (DPV) experiments were done for different concentrations of methyldopa (Fig. 6). The oxidation peak currents of methyldopa, at the surface of a modified electrode, were proportional to the concentration of the methyldopa within the ranges 0.5 to 800.0 μM. The detection limit

(3σ) of methyldopa was found to be 2.3×10^{-7} M. Table I shows a comparison of the analytical figures of merit, of the proposed method, with the different reported techniques for the determination of methyldopa.

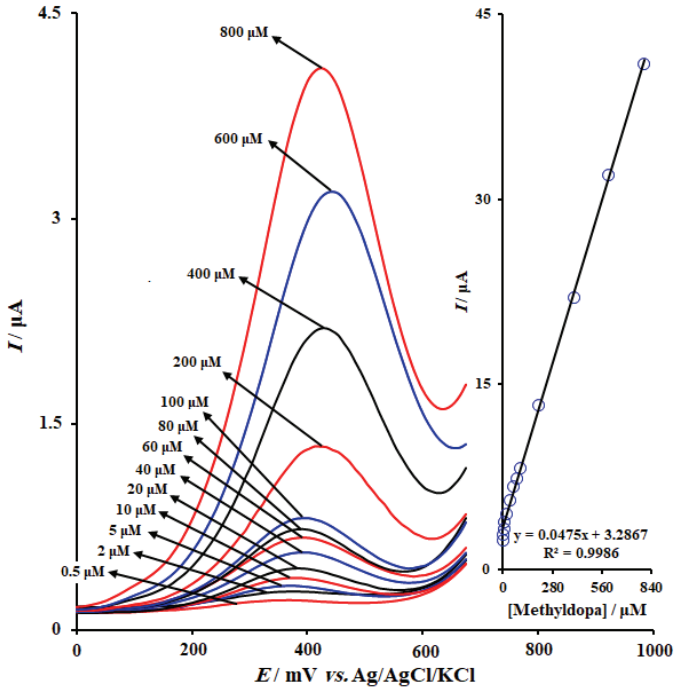

Fig. 6. DPVs of Cu/TiO_2/GCE in 0.1 M PBS (pH 7.0) containing different concentrations of methyldopa (0.5, 2.0, 5.0, 10.0, 20.0, 40.0, 60.0, 80.0, 100.0, 200.0, 400.0, 600.0 and 800.0 µM of methyldopa). Inset: a plot of the electrocatalytic peak current as a function of methyldopa concentration in the range of 0.5–800.0 µM.

Interference studies

The influence of various substances as compounds potentially interfering with the determination of methyldopa was studied under optimum conditions. The potentially interfering substances were chosen from the group of substances commonly found with methyldopa in pharmaceuticals and/or in biological fluids. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error of less than ±5 % in the determination of methyldopa. According to the results, L-lysine, glucose, NADH, acetaminophen, uric acid, L-asparagine, L-serine, L-threonine, L-proline, L-histidine, L-glycine, L-tryptophan, L-phenylalanine, lactose, tyrosine, saccarose, fructose, benzoic acid, methanol, ethanol, urea, caffeine, Mg^{2+}, Al^{3+}, NH_4^+, F^-, SO_4^{2-} and S^{2-} did not show interference in the determination of methyldopa.

TABLE I. Comparison of the efficiency of some methods used in detection of methyldopa

Method	Modifier	*LOD*	*LDR*	Ref.
Gas chromatography-electron capture negative ion mass spectrometry	–	99.1 nM/L	–	43
High-performance liquid chromatographic	–	0.014 μg/L	200.0–10000.0 ng/ml	44
High-performance liquid chromatographic	–	-	50.0–6000.0 ng/ml	45
Voltammetry	CdSe@Ag_2Se core–shell fluorescent quantum dots	0.04 μM	0.09–60.0 μM	46
Voltammetry	Fluorine doped SnO_2 substrates	2.9 μM	0.2–60.0 μM	47
Voltammetry	Multi-walled carbon nanotubes	1.0 nM	0.005–0.388 μM	48
Voltammetry	TiO_2 nanoparticles and ferrocene monocarboxylic acid	0.08 μM	0.02–100.0 μM	49
Voltammetry	5-Amino-2′-ethyl-biphenyl--2-ol and carbon nanotubes	48.0 nM	0.1–210.0 μM	50
Voltammetry	Ionic liquid	5.5 μM	34.8–370.3 μM	51
Voltammetry	Cu/TiO_2 nanocomposite	0.23 μM	0.5–800.0 μM	This work

Real sample analysis

In order to evaluate the analytical applicability of the proposed method, it was also applied to the determination of methyldopa in methyldopa tablets and urine samples. The results for determination of the methyldopa in real samples are given in Table II. The satisfactory recovery of the experimental results was found for methyldopa. The reproducibility of the method was demonstrated by the mean relative standard deviation (*RSD*).

TABLE II. The application of Cu/TiO_2/GCE for determination of methyldopa in methyldopa tablet and urine samples (n = 5). All concentrations are in μM

Sample	Spiked	Found	Recovery, %	*RSD* / %
Methyldopa tablet	0	–	–	–
	5.0	4.9	98.0	2.7
	10.0	10.3	103.0	3.4
	15.0	15.2	101.3	1.9
	20.0	19.8	99.0	2.4
Urine	0	–	–	–
	7.5	7.4	98.7	3.2
	12.5	12.6	100.8	2.4
	17.5	17.7	101.1	1.8
	22.5	22.3	99.1	2.8

CONCLUSIONS

Cu/TiO_2-modified GCE shows an excellent synergic behaviour towards the methyldopa oxidation in an aqueous phosphate buffer (pH 7.0) solution. Our study showed that in the case of the unmodified GCE, the voltammogram of methyldopa exhibit just a small hump peak, but after modification of the electrode with Cu/TiO_2 nanocomposite, the oxidation peak current of methyldopa is significantly enhanced. This technique offers a number of advantages, compared to the other published electrochemical methods, such as simplicity in the preparation of the modified electrode and its high selectivity. The modified electrode represents appropriate performance in detecting methyldopa and exhibits excellent stability and reproducibility. In the differential pulse voltammetric determination, the detection limit of methyldopa was estimated at 0.23 μM. Based on the electrochemical oxidation, the quantitative determination of methyldopa in pharmaceutical dosage and biological fluids samples was developed by a simple, rapid, selective and sensitive DPV technique. These properties indicate that the Cu/TiO_2-modified electrode is a good electrochemical sensor for the determination of methyldopa. According to the available data, this method has appropriate properties compared to the previous studies such as high selectivity, sensitivity, low detection limit and wide linear dynamic range.

ИЗВОД

ЕЛЕКТРОХЕМИЈСКИ СЕНЗОР ЗА МЕТИЛДОПУ НА БАЗИ ЕЛЕКТРОДЕ ОД СТАКЛАСТОГ УГЉЕНИКА МОДИФИКОВАНЕ НАНОКОМПОЗИТОМ Cu/TiO_2

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Електрода од стакластог угљеника је модификована нанокомпозитом Cu/TiO_2 (Cu/TiO_2/GCE) у циљу детекције метилдопе, методама цикличне волтаметрије и диференцијалне пулсне волтаметрије. У поређењу са немодификованим стакластим угљеником, електрода Cu/TiO_2/GCE је показала одличну електрохемијску активност за оксидацију метилдопе. Калибрациони дијаграм одређен диференцијалном пулсном волтаметријом показао је линеарност у опсегу концентрација од 0,5 до 800,0 μM и границу детекције ($S/N = 3$) од 0,23 μM. Поред тога, електрохемијски сензор Cu/TiO_2/GCE се показао погодним за одређивање метилдопе у таблетама и узорцима урина.

(Примљено 30. септембра 2017, ревидирано 17. јануара, прихваћено 29. јануара 2018)

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