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Application of a modified graphene nanosheet paste electrode for voltammetric determination of methyl dopa in urine and pharmaceutical formulation

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Abstract

Background: Electrochemical sensors and biosensors for pharmaceutical, food, agricultural and environmental analyses have been growing rapidly due to electrochemical behavior of drugs and biomolecules and partly due to advances in electrochemical measuring systems. In the present work, we describe the preparation of a new electrode composed of graphene (G) modified with 2,7-bis(ferrocenyl ethyl) fluorene-9-one (2,7-BFGPE) and investigate its performance for the electrocatalytic determination of methyl dopa in aqueous solutions.

Methods: Experimental section was carried out using cyclic voltammetry, square wave voltammetry and chronoamperometry.

Results: Under the optimized conditions (pH 7.0), the square wave voltammetric peak current of methyl dopa increased linearly with methyl dopa concentration in the ranges of 9.0×10^{-8} to 5.0×10^{-4} M. The detection limit was 5.0×10^{-8} M methyl dopa. The diffusion coefficient ($D = 9.35 \times 10^{-6}$ cm²/s) and electron transfer coefficient ($\alpha = 0.52$) for methyl dopa oxidation were also determined.

Conclusions: The method shows the development of a sensor for selective and sensitive determination of methyl dopa. This sensor was successfully applied to determine the methyl dopa in some real samples.

Keywords: Methyl dopa; Graphene nanosheets; Modified electrode; Voltammetry; Electrochemical sensor

Background

Methyl dopa is an antihypertensive agent that is used in the treatment of high blood pressure or hypertension, especially when it is complicated with renal disease. Its antihypertensive properties are primarily due to its action on the central nervous system. Methyl dopa inhibits the enzyme DOPA decarboxylase, which converts L-DOPA into dopamine, and is a precursor for norepinephrine and subsequently epinephrine. It is converted to α -methyl norepinephrine in adrenergic nerve terminals, and its antihypertensive action appears to be due to its stimulation of central adrenal receptors, which reduces sympathetic tone

and produces a fall in blood pressure. The therapeutic concentration of methyl dopa in human plasma is usually in the range of 0.1 to 0.5 mg L⁻¹, and its average terminal elimination half-life is 2 h (Kwan et al. 1976; Myhre et al. 1982). Clearly, detection and quantification of methyl dopa is an important feature in pharmaceutical and clinical procedures (Rezaei et al. 2013; Gholivand and Amiri 2013). Several analytical procedures have been reported for the analysis of methyl dopa in bulk form, pharmaceutical form, or biological fluids. These include titrimetry, chromatography, kinetic methods, spectrophotometry, and H NMR. However, these methods have disadvantages, including high costs, long analysis times, the requirement of complex and tedious sample pretreatments, and, in some cases, a low sensitivity and selectivity, that make them unsuitable for a routine analysis. On the other hand, electrochemical methods have attracted great interest because of

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their simplicity, rapidness, and high sensitivity in detecting methyl dopa and various other analytes without requiring tedious pretreatments (Athanasios-Malaki and Koupparis 1984; Tajik et al. 2013a; Shahrokhian and Rastgar 2011; Molaakbari et al. 2014; Moccelini et al. 2011).

The use of carbon paste as an electrode was initially reported in 1958 by Adams. In afterward researches, a wide variety of modifiers including enzymes, polymers, and nanomaterials have been used with these versatile electrodes. Carbon paste electrodes (CPEs) are widely applicable in both electrochemical studies and electroanalysis, thanks to their advantages such as very low background current (compared to solid graphite or noble metal electrodes), facility to prepare, low cost, large potential window, simple surface renewal process, and easiness of miniaturization. Besides the advantageous properties and characteristics listed previously, the feasibility of incorporating different substances during paste preparation (which results in the so-called modified carbon paste electrode) allows the fabrication of electrodes with desired composition and, hence, with predetermined properties (Tajik et al. 2013b; Khoobi et al. 2013; Mokhtari et al. 2012; Díaz et al. 2013; Gholivand and Mohammadi-Behzad 2014; Mazloun-Ardakani et al. 2010; Thomas et al. 2013a; Raouf et al. 2007; Dönmez et al. 2014; Raouf et al. 2006a).

Electrochemical methods using chemically modified electrodes (CMEs) have been widely used as sensitive and selective analytical methods for the detection of trace amounts of biologically important compounds. One of the most important properties of CMEs is their ability to catalyze the electrode process via the significant decrease of overpotential with respect to the unmodified electrode. With respect to the relatively selective interaction of the electron mediator with the target analyte in a coordinated fashion, these electrodes are capable of considerably enhancing the selectivity of electroanalytical methods (Beitollahi et al. 2011a; Luo et al. 2013; Taleat et al. 2008; Huo et al. 2013; Thomas et al. 2013b; Raouf et al. 2006b; Oliveira et al. 2013; Beitollahi et al. 2011b; Thomas et al. 2013c; Mohammadi et al. 2013; Sanghavi et al. 2013; Beitollahi et al. 2014; Li et al. 2012; Ghoreishi et al. 2012; Yildiz et al. 2014).

As a new kind of two-dimensional carbon material, graphene has attracted increasing attention due to its unique properties including high surface area, excellent electrical conductivity, quick electron mobility at room temperature, high mechanical strength, and ease for functionalization (Joon et al. 2014). Graphene-based electrochemical sensors have been proved to possess excellent electrocatalytic ability and good performances (Ping et al. 2014; Ma et al. 2014; Silva et al. 2014; Zhu et al. 2013; Sun et al. 2012; Xi et al. 2013).

In the present work, we describe the preparation of a new electrode composed of graphene (G) modified with

2,7-bis(ferrocenyl ethyl)fluoren-9-one (2,7-BFGPE) and investigate its performance for the electrocatalytic determination of methyl dopa in aqueous solutions.

Methods

Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT-302 N, Eco Chemie, Utrecht, The Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. A conventional three-electrode cell was used at $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and 2,7-BFGPE were used as the reference, auxiliary, and working electrodes, respectively. A Metrohm 691 pH/Ion Meter (Utrecht, The Netherlands) was used for pH measurements.

All solutions were freshly prepared with double-distilled water. Methyl dopa and all other reagents were of analytical grade from Merck (Darmstadt, Germany). Graphite powder and paraffin oil (DC 350, density = 0.88 g cm^{-3}) as the binding agent (both from Merck) were used for preparing the pastes. The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0 to 11.0. 2,7-BF was synthesized in our laboratory as reported previously (Raouf et al. 2006a).

Synthesis of graphene nanosheets

Graphene nanosheets were synthesized from natural graphite flakes based on the modified Hummers and Offeman's method (Hummers and Offeman 1958). In a typical synthesis process, 1.0 g of pristine graphite flakes was immersed in 50 mL of formic acid and then sonicated for 2 h at room temperature. The resulting graphite plates were washed with acetone and then dried in an oven at 95°C for 12 h. Then, 100 mL H_2SO_4 (95%) was added into a 500-mL flask and cooled by immersion in an ice bath followed by stirring. About 1.0 g of treated graphite powder and 0.5 g NaNO_3 were added under vigorous stirring to avoid agglomeration. After the graphite powder was well dispersed, 3 g KMnO_4 was added gradually under stirring and cooling so that the temperature of the mixture was maintained below 10°C . The mixture was stirred for 2 h and diluted with deionized double-distilled water (in an ice bath). After that, 25 mL 15% H_2O_2 was slowly added to the mixture until the colour of the mixture changed to brilliant yellow, indicating fully oxidized graphite. The as-obtained graphite oxide slurry was re-dispersed in deionized double-distilled water and then exfoliated to generate graphene oxide nanosheets by sonication for 2 h. Then, the solution was filtered and washed with diluted HCl solution to remove metal ions. Finally, the product was washed with deionized double-distilled water until the solution became acid free and dried under vacuum at 50°C . A typical transmission

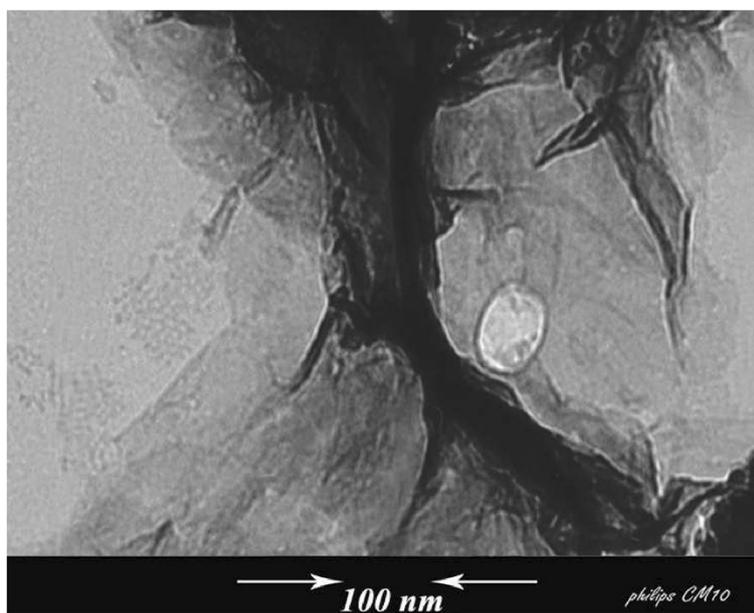


Figure 1 TEM image of the synthesized graphene nanosheets.

electron microscopy (TEM) image of the synthesized graphene nanosheets is shown in Figure 1.

Preparation of the electrode

2,7-BFGPEs were prepared by hand-mixing 0.01 g of 2,7-BF with 0.89 g graphite powder and 0.1 g G with a mortar and pestle. Then, approximately 0.7 mL of paraffin was added to the above mixture and mixed for 20 min until a uniformly wetted paste was obtained. The paste was then packed into the end of a glass tube (ca. 3.4 mm i.d. and 10 cm long). A copper wire inserted into the carbon paste provided the electrical contact. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing with a weighing paper.

For comparison, 2,7-BF-modified CPE (2,7-BFCPE) without G, G paste electrode (GPE) without 2,7-BF, and unmodified CPE in the absence of both 2,7-BF and G were also prepared in the same way.

Results and discussion

Electrochemical behavior of 2,7-BFGPE

2,7-BFGPE was constructed and its electrochemical properties were studied in a 0.1 M phosphate-buffered saline (PBS; pH 7.0) by cyclic voltammetry (CV). The experimental results show well-defined and reproducible anodic and cathodic peaks related to the 2,7-bis(ferrocenyl ethyl)fluoren-9-one/2,7-bis(ferricenium ethyl)fluoren-9-one redox system, with E_{pa} , E_{pc} , and E' of 320, 260, and 290 mV vs. Ag/AgCl/KCl (3.0 M) respectively. The observed peak separation potential ($\Delta E_p = E_{pa} - E_{pc}$) of 60 mV was greater than the value of $59/n$ mV expected for a reversible system (Bard and Faulkner 2001), suggesting that the redox couple

of 2,7-BF in 2,7-BFGPE has a quasi-reversible behavior in aqueous medium.

In addition, the long-term stability of 2,7-BFGPE was tested over a 3-week period. When CVs were recorded after the modified electrode was stored in atmosphere at room temperature, the peak potential for methyl dopa oxidation

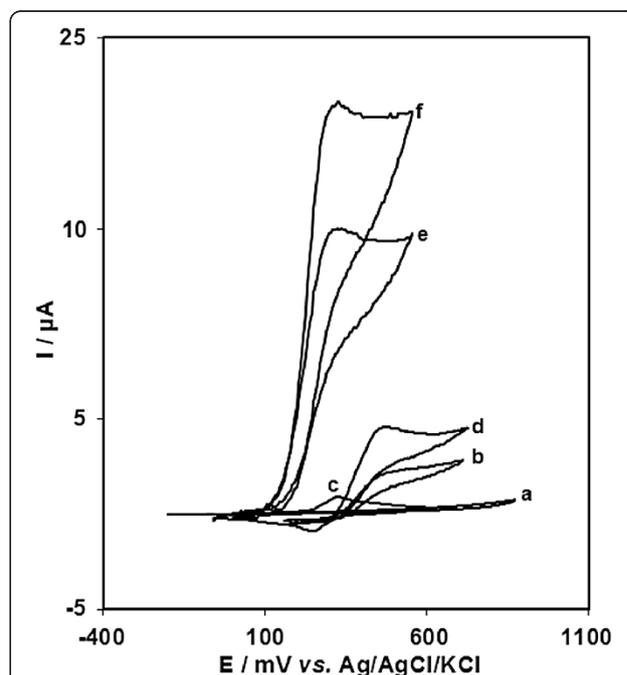
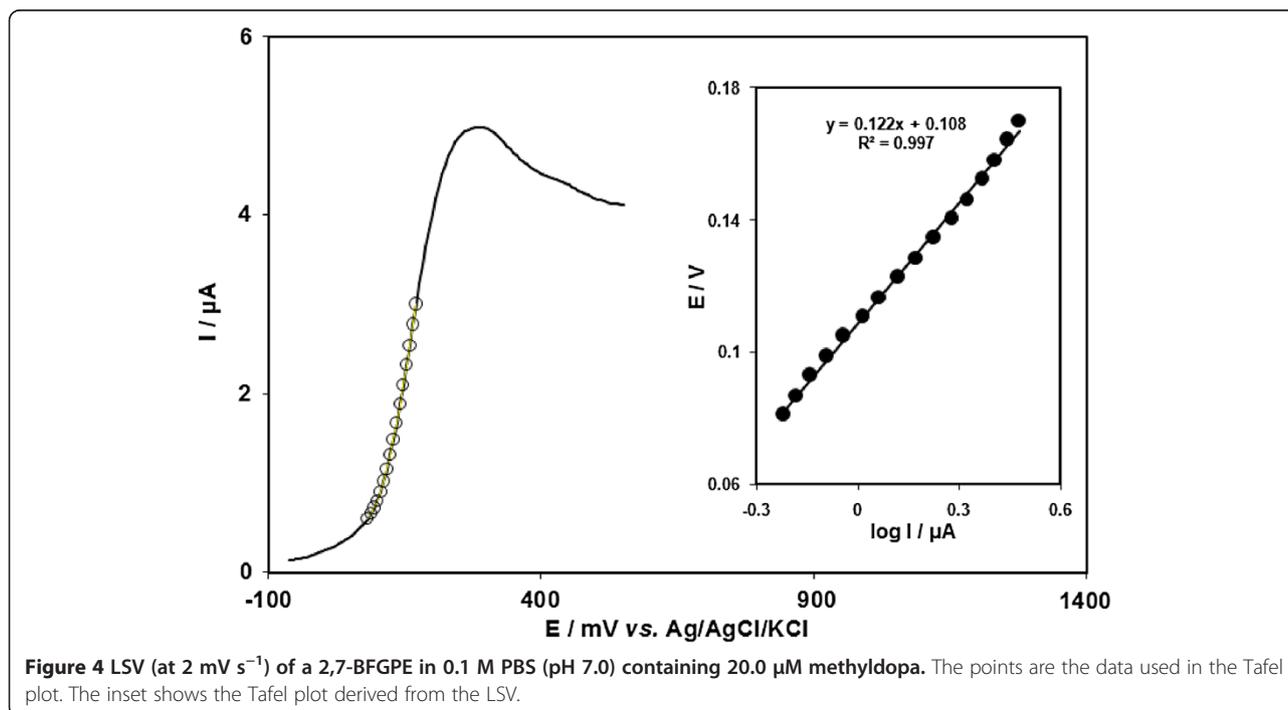
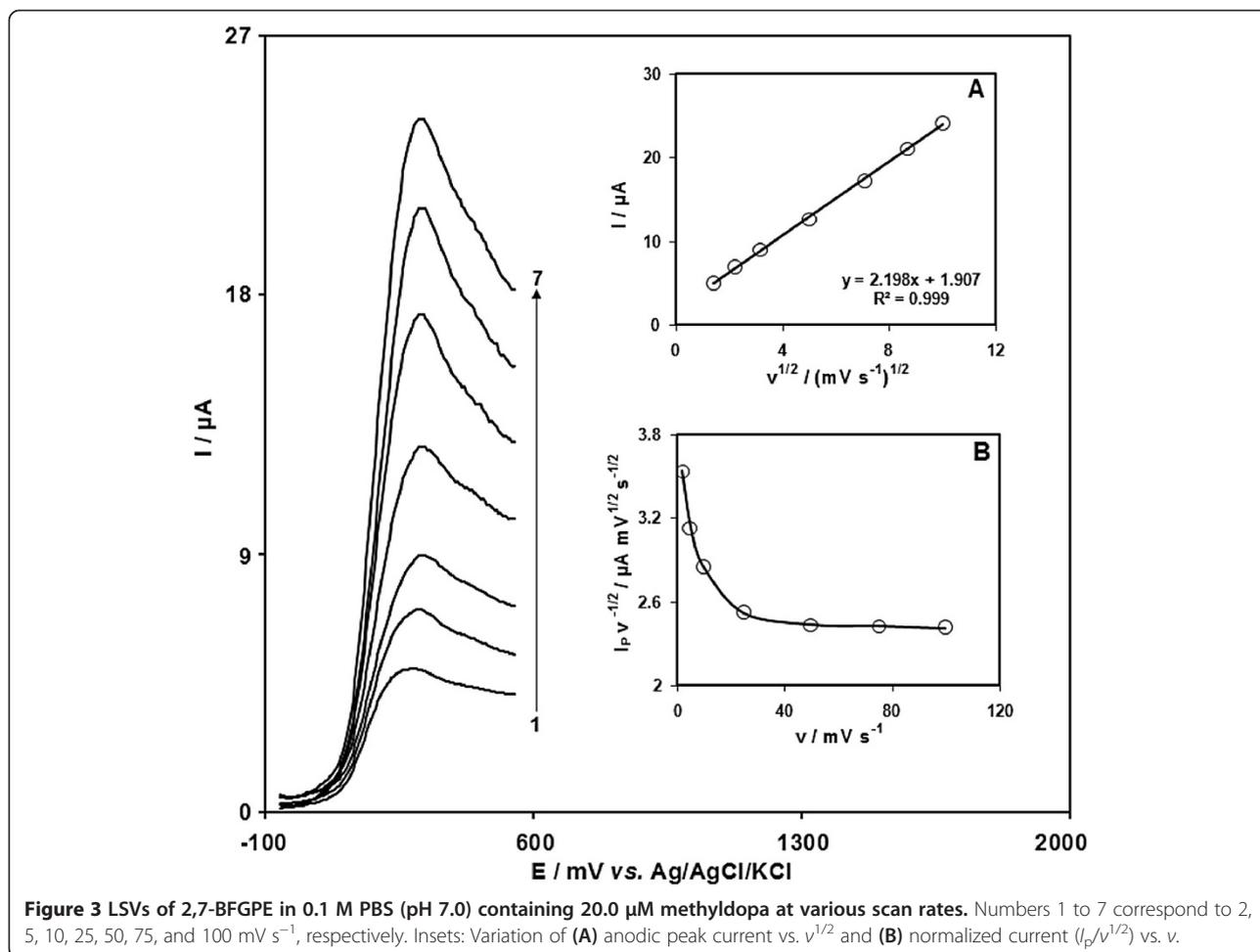
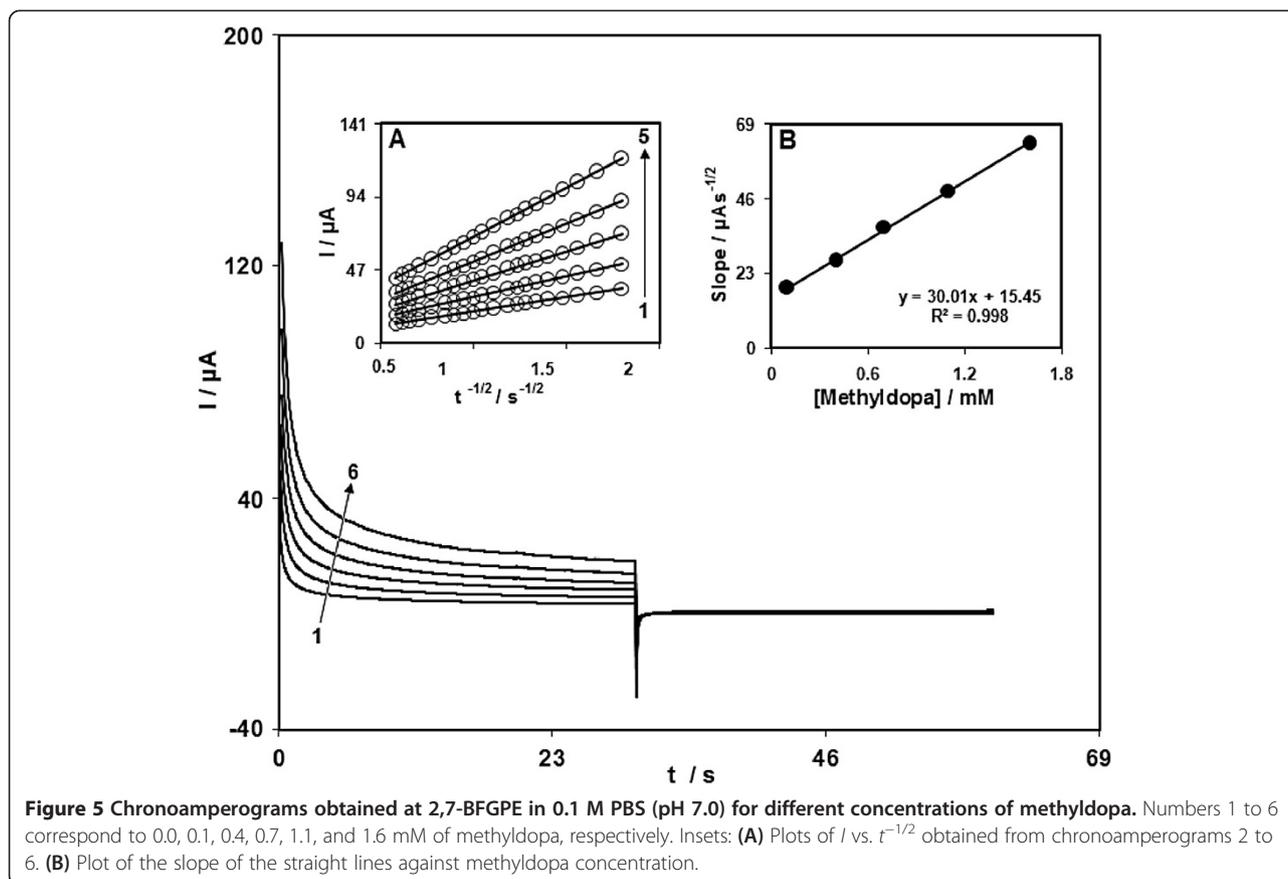


Figure 2 CV responses. (a) Unmodified CPE in 0.1 M PBS (pH 7.0) at scan rate of 10 mV s^{-1} . (b) As (a) + 0.35 mM methyl dopa. (c) As (a) at the surface of 2,7-BFGPE. (d) As (b) at the surface of GPE. (e) As (b) at the surface of 2,7-BFCPE. (f) As (b) at the surface of 2,7-BFGPE.





was unchanged and the current signals showed less than 2.1% decrease relative to the initial response. The antifouling properties of the modified electrode toward methyl dopa oxidation and its oxidation products were investigated by recording the cyclic voltammograms of the modified electrode before and after use in the presence of methyl dopa. Cyclic voltammograms were recorded in the presence of methyl dopa after having cycled the potential 20 times at a scan rate of 10 mV s^{-1} . The peak potentials were unchanged, and the currents decreased by less than 2.3%. Therefore, at the surface of 2,7-BFGPE, not only the sensitivity increased, but the fouling effect of the analyte and its oxidation product also decreased.

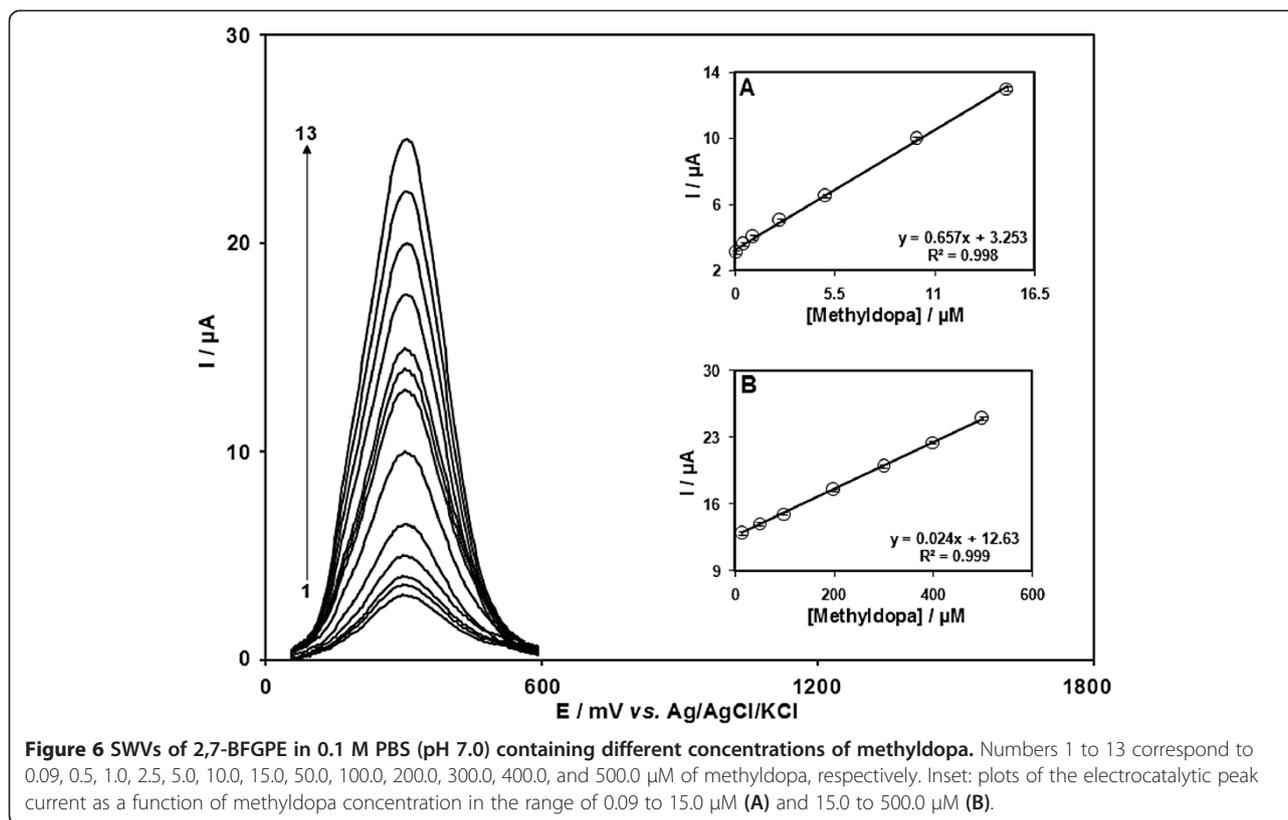
Influence of pH

The electrochemical behavior of methyl dopa is dependent on the pH value of the aqueous solution, whereas the electrochemical properties of the 2,7-bis(ferrocenyl ethyl) fluoren-9-one/2,7-bis(ferricenium ethyl)fluoren-9-one (Fc/Fc⁺) redox couple are independent on pH. Therefore, pH optimization of the solution seems to be necessary in order to obtain the electrocatalytic oxidation of methyl dopa. Thus, the electrochemical behavior of methyl dopa was studied in 0.1 M PBS in different pH values ($2.0 < \text{pH} < 11.0$) at the surface of 2,7-BFGPE by CV. It was found

that the electrocatalytic oxidation of methyl dopa at the surface of 2,7-BFGPE was more favored under neutral conditions than in acidic or basic medium. This appears as a gradual growth in the anodic peak current and a simultaneous decrease in the cathodic peak current in the CVs of 2,7-BFGPE. Thus, pH 7.0 was chosen as the optimum pH for electrocatalysis of methyl dopa oxidation at the surface of 2,7-BFGPE.

Electrocatalytic oxidation of methyl dopa at a 2,7-BFGPE

Figure 2 depicts the CV responses for the electrochemical oxidation of 0.35 mM methyl dopa at the unmodified CPE (curve b), GPE (curve d), 2,7-BFCPE (curve e), and 2,7-BFGPE (curve f). As it is seen, while the anodic peak potential for methyl dopa oxidation at the GPE and unmodified CPE are 480 and 520 mV, respectively, the corresponding potential at 2,7-BFGPE and 2,7-BFCPE is approximately 320 mV. These results indicate that the peak potential for methyl dopa oxidation at 2,7-BFGPE and 2,7-BFCPE shift by approximately 160 and 200 mV toward negative values compared to GPE and unmodified CPE, respectively. However, 2,7-BFGPE shows much higher anodic peak current for the oxidation of methyl dopa compared to 2,7-BFCPE, indicating that the combination of G and the mediator (2,7-BF) has



significantly improved the performance of the electrode toward methyldopa oxidation. In fact, 2,7-BFGPE, in the absence of methyldopa, exhibited a well-behaved redox reaction (Figure 2, curve c) in 0.1 M PBS (pH 7.0). However, there was a drastic increase in the anodic peak current in the presence of 0.35 mM methyldopa (curve f), which can be related to the strong electrocatalytic effect of 2,7-BFGPE toward this compound (Bard and Faulkner 2001).

The effect of scan rate on the electrocatalytic oxidation of methyldopa at 2,7-BFGPE was investigated by linear sweep voltammetry (Figure 3). As can be observed in Figure 3, the oxidation peak potential shifted to more positive potentials with increasing scan rate, confirming the kinetic limitation in the electrochemical reaction. Also, a plot of peak height (I_p) vs. the square root of scan rate ($\nu^{1/2}$) was found to be linear in the range of 2 to 100 mV s^{-1} , suggesting that, at

sufficient overpotential, the process is diffusion- rather than surface-controlled (Figure 3A) (Bard and Faulkner 2001). A plot of the scan rate-normalized current ($I_p/\nu^{1/2}$) vs. scan rate (Figure 3B) exhibits the characteristic shape typical of an EC process (Bard and Faulkner 2001).

Figure 4 shows the linear sweep voltammograms (LSVs) of an 2,7-BFGPE obtained in 0.1 M PBS (pH 7.0) containing 20.0 μM methyldopa, with a sweep rate of 2 mV s^{-1} . The points show the rising part of the voltammogram (known as the Tafel region), which is affected by the electron transfer kinetics between methyldopa and 2,7-BFGPE. If deprotonation of methyldopa is a sufficiently fast step, the number of electrons involved in the rate-determining step can be estimated from the slope of the Tafel plot. The inset of Figure 4 shows a Tafel plot that was drawn from points of the Tafel region of the LSV. The Tafel slope of

Table 1 Comparison of the efficiency of some modified electrodes used in the electrocatalysis of methyldopa

Electrode	Modifier	Method	pH	Dynamic range (M)	Limit of detection (M)	Reference
Carbon paste	Ferrocene monocarboxylic acid	Voltammetry	7.0	2.0×10^{-7} to 1.0×10^{-4}	8.0×10^{-8}	Molaakbari et al. (2014)
Glassy carbon	Pt-Ru nanoparticles	Voltammetry	3.0	5.0×10^{-8} to 4.0×10^{-5}	1.0×10^{-8}	Shahrokhian and Rastgar (2011)
Carbon paste	Cellulose acetate/ionic liquids	Voltammetry	5.5	3.48×10^{-5} to 3.7×10^{-4}	5.5×10^{-6}	Moccelini et al. (2011)
Carbon nanotube paste	5AEB	Voltammetry	8.0	1.0×10^{-7} to 2.1×10^{-4}	4.8×10^{-8}	Tajik et al. (2013a)
Graphene paste	2,7-BF	Voltammetry	7.0	8.0×10^{-8} to 5.0×10^{-4}	5.0×10^{-8}	This work

Table 2 The application of 2,7-BFGPE for determination of methyl dopa in methyl dopa tablet and urine samples

Sample	Original content	Spiked	Found	Recovery (%)	R.S.D. (%)
Methyl dopa tablet	15.0	0	15.3	102.0	3.5
	15.0	5.0	19.8	99.0	1.9
	15.0	1.0	24.4	97.6	2.5
	15.0	15.0	30.5	101.7	2.9
Urine	-	7.5	7.4	98.7	1.8
	-	12.5	12.9	103.2	3.1
	-	17.5	17.4	99.4	2.3
	-	22.5	23.1	102.7	2.6

All concentrations are in micromolar ($n = 5$).

0.122 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 $\alpha = 0.52$ (Bard and Faulkner 2001).

Chronoamperometric measurements

Chronoamperometric measurements of methyl dopa at 2,7-BFGPE were carried out by setting the working electrode potential at 0.4 V (at the first potential step) and at 0.1 V (at the second potential step) vs. Ag/AgCl/KCl (3.0 M) for the various concentrations of methyl dopa in buffered aqueous solutions (pH 7.0) (Figure 5). For an electroactive material (methyl dopa in this case) with a diffusion coefficient of D , the current observed for the electrochemical reaction at the mass transport-limited condition is described by the Cottrell equation (Bard and Faulkner 2001). Experimental plots of I vs. $t^{-1/2}$ were employed, with the best fits for different concentrations of methyl dopa (Figure 5A). The slopes of the resulting straight lines were then plotted vs. the methyl dopa concentration (Figure 5B). From the resulting slope and Cottrell equation, the mean value of D was found to be $9.35 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

Calibration plot and limit of detection

The Square Wave Voltammetry (SWV) method was used to determine the concentration of methyl dopa (initial potential = 0.06 V, end potential = 0.6 V, step potential = 0.001 V, amplitude = 0.02 V, frequency = 10 Hz) (Figure 6). The plot of peak current vs. methyl dopa concentration consisted of two linear segments with slopes of 0.657 and 0.024 $\mu\text{A } \mu\text{M}^{-1}$ in the concentration ranges of 0.09 to 15.0 μM and 15.0 to 500.0 μM , respectively. The decrease in sensitivity (slope) of the second linear segment is likely due to kinetic limitation (Bard and Faulkner 2001). The detection limit (3σ) of methyl dopa was found to be 50.0 nM. These values are comparable with values reported by other research groups for electrocatalytic oxidation of

methyl dopa at the surface of chemically modified electrodes by other mediators (Table 1).

Interference studies

The influence of various substances as compounds potentially interfering with the determination of methyl dopa was studied under optimum conditions. The potentially interfering substances were chosen from the group of substances commonly found with methyl dopa 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 $\pm 5\%$ in the determination of methyl dopa. 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, saccharose, fructose, benzoic acid, methanol, ethanol, urea, caffeine, Mg^{2+} , Al^{3+} , NH_4^+ , Fe^{2+} , Fe^{3+} , F^- , SO_4^{2-} , and S^{2-} did not show interference in the determination of methyl dopa. However, levodopa, carbidopa, dopamine, and ascorbic acid with equal molar concentration make interference. Although ascorbic acid showed interference, this interference could be minimized, if necessary, by using ascorbic oxidase enzyme, which exhibits a high selectivity to the oxidation of ascorbic acid.

Real sample analysis

Determination of methyl dopa in methyl dopa tablet and urine samples

In order to evaluate the analytical applicability of the proposed method, it was also applied for the determination of methyl dopa in methyl dopa tablet (each tablet containing 250 mg methyl dopa from Darou-Pakhsh, Tehran, Iran). The results for determination of methyl dopa in the methyl dopa tablet are given in Table 2. Satisfactory recovery of the experimental results was found for methyl dopa. The reproducibility of the method was demonstrated by the mean relative standard deviation (R.S.D.).

Also, in order to evaluate the analytical applicability of the proposed method, it was applied for the determination of methyl dopa in urine samples. Known amounts of methyl dopa were added to the urine sample, and its concentrations were estimated with the proposed method. The urine sample was found to be free from methyl dopa. Therefore, different amounts of methyl dopa were spiked to the sample and analyzed by the proposed method. The results for determination of methyl dopa in real samples are given in Table 2. Satisfactory recovery of the experimental results was found for methyl dopa. The reproducibility of the method was demonstrated by the mean R.S.D.

Conclusions

2,7-BFGPE was prepared and used for the investigation of the electrochemical behavior of methyl dopa. Two pairs of

well-defined redox peaks were obtained at 2,7-BFGPE. 2,7-BFGPE showed excellent electrocatalytic activity for the redox of methyl dopa. Compared with the bare electrode, the oxidation current of methyl dopa increased greatly and the oxidation peak potential shifted negatively by 200 mV. This sensor showed a wide linear range (0.09 to 500.0 μM) with good detection limit (0.05 μM) for methyl dopa. This sensor was successfully applied to determine methyl dopa in some real samples.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

Hadi Beitollahi, Somayeh Tajik and Hossein Asadi performed the fields of experimental sections and analysis of data. Pourya Biparva synthesized the graphene nanosheets. All authors read and approved the final manuscript.

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