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Full Paper

Electrochemical Sensing of Isoproterenol using Graphite Screen-printed Electrode Modified with Graphene Quantum Dots

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Abstract- The graphene quantum dots (GQDs) were prepared by tuning the carbonization degree of citric acid and graphite screen-printed electrode modified with graphene quantum dots (GQDs/SPE) was constructed and used for the sensitive voltammetric determination of isoproterenol. In comparison with unmodified electrode, the presence of the GQD/ SPE resulted in a remarkable increase in the peak currents. The electrochemical response characteristics of the modified electrode toward isoproterenol were studied by means of cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometry. It was demonstrated that the modified electrode presents good electrical conductivity and has favorable electrochemical response to isoproterenol. The (GQDs/SPE) displays a linear range from 1.0 to 900.0 μM and a detection limit of 0.6 μM (S/N=3) to isoproterenol.

Keywords- Isoproterenol, Graphite screen-printed electrode, Graphene quantum dots, Modified electrode

1. INTRODUCTION

Isoproterenol is a β-adrenergic receptor agonist. Isoproterenol is a catecholamine drug widely used for hypertension and allergic emergencies, bronchitis, cardiac shock and heart

attack [1-4]. Isoproterenol has positive inotropic and chronotropic effects on the heart and is used for bradycardia or heart block, but overdose of the drug may cause heart failure and arrhythmias [5,6]. Isoproterenol is readily absorbed when given parenterally or as an aerosol. Absorption of sublingual or oral doses is unreliable. The drug is poorly absorbed from stomach, but well absorbed from small intestine, proximal colon, and rectum and from the mucous membrane of the trachea. It is recognized that the dosage requirements for isoproterenol vary widely according to the route of administration; when the drug is given intravenously pharmacological effects are seen with only few micrograms [7], whereas using the oral route, tablets containing 180–360 mg are required daily to control chronic heart block [8]. Some important pathophysiological changes observed after isoproterenol induction are increased oxygen consumption, raised intracellular pH and calcium levels, alterations in membrane permeability, increased lipid peroxidation, increased expression of cell death inducible proteins, ultimately leading to necrosis and death of the myocytes [9,10].Thus Various analytical methods have been reported for detection of isoproterenol for example, high performance liquid chromatography [11], chemiluminescence [12], spectrophotometry [13], capillary electrophoresis [14,15]. However, these methods have some disadvantages such as low sensitivity and poor selectivity, time-consuming pretreatment and expensive protocols [16,17]. The electrochemical technique is attractive because of its high sensitivity, low cost, rapid and simplicity thus used for determination of isoproterenol [18-21]. The chemically modified electrodes have been widely used as sensitive and favorable analytical methods for determination of isoproterenol [22]

In the electrochemical method, modified electrodes with nanomaterials because of their unique physical and chemical properties have some advantages such as long term stability, sensitivity, reduced over potential, facilitate in easy electrode reaction involving transfer of electrons and homogeneity in electro-analysis [23-30].

The use of screen-printed electrodes (SPEs) instead of conventional electrodes, such as carbon paste or glassy carbon electrodes, contributes to show some trends in analytical chemistry such as miniaturization [31,32]. Electrochemical sensors based on SPEs meet the requirements of in situ screening devices in that all the equipment needed for electrochemical analysis is portable. Screen-printed electrodes have all the major performance characteristics of sensors: sample preparation is minimal; they are quick, cheap, and easy to use; and they are small and can be miniaturized with new technology [33-36].

Graphene quantum dots (GQDs) are zero-dimensional nanomaterials with lateral size less than 100 nm and consisted of a single layer or few-layer of carbon atoms in a closely packed honeycomb structure [37]. Graphene quantum dots possessing high electrical conductivity, large surface area, biocompatibility, low toxicity, good thermal conductivity, excellent photoluminescence, good water solubility and chemical inertness [38-41], and thus have been gained many applications in optical sensing platforms [42],bio imaging [43], drug delivery [44],

photovoltaic devices [45]and lithium ion batteries [46]. In addition, GQDs have been recognized as both excellent electron donors and acceptor, making them interesting candidates for producing electrode materials and result the graphene quantum dots are using as sensing materials in electrochemical detections [47].

In the present work, the GQDs -modified SPEs were used for the first time as a simple, inexpensive, rapid and sensitive electrochemical sensor for determination of isoproterenol and in pharmaceutical formulations and human fluids. The SPEs showed high sensitivity for determination of isoproterenol in real samples.

2. EXPERIMENTAL

2.1. Chemicals and apparatus

To perform the electrochemical experiments an Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands) was used and the system was controlled using a general purpose electrochemical system software. The screen-printed electrode (DropSens, DRP-110, Spain) consists of three main parts which are a graphite counter electrode, a silver pseudo-reference electrode and a graphite working electrode. A Metrohm 710 pH meter was used for pH measurements.

Isoproterenol and all other reagents were analytical grade, and were obtained from Merck (Darmstadt, Germany), and the orthophosphoric acid and its salts were used to prepare buffers in the pH range of 2.0–9.0.

2.2. Synthesis of Graphene quantum dots

Graphene quantum dots were prepared by directly pyrolyzing citric acid. In a typical synthesis, 2 g citric acid monohydrate was put into a ceramic crucible and heated to 200 °C in a muffle furnace. After 35 min, the muffle furnace was gradually cooled down to room temperature and brown GQDs powders were obtained.

2.3. Preparation of the electrode

The bare screen-printed electrode was coated with GQDs as follows. A stock solution of GQDs in 1 mL aqueous solution was prepared by dispersing 1 mg GQDs with ultrasonication for 45 min, and a 5 µl aliquot of the GQDs/H_2O suspension solution was casted on the carbon working electrodes, and waiting until the solvent was evaporated in room temperature.

2.4. Preparation of real samples

One milliliter of an isoproterenol ampoule was diluted to 10 mL with 0.1 M PBS (pH 7.0); then, different volume of the diluted solution was transferred into each of a series of 25

mL volumetric flasks and diluted to the mark with PBS. The isoproterenol content was analyzed by the proposed method using the standard addition method.

Urine samples were stored in a refrigerator immediately after collection. Ten millilitres of the samples were centrifuged for 15 min at 2000 rpm. The supernatant was filtered out by using a 0.45 µm filter. Next, different volumes of the solution was transferred into a 25 mL volumetric flask and diluted to the mark with PBS (pH 7.0). The diluted urine samples were spiked with different amounts of isoproterenol. The isoproterenol contents were analysed by the proposed method by using the standard addition method.

3. RESULT AND DISCUSSION

3.1. Electrochemical profile of the analytes on the GO/GCE

Due to the fact that the electrochemical behaviour of isoproterenol is pH-dependent optimizing the pH of the solution is necessary for obtaining the best results. Hence, the evaluations were performed in different pH values ranging from 2.0–9.0, and the results showed that the best results during the electro-oxidation of isoproterenol at the surface of the modified electrodes could be obtained at pH=7.0. Fig. 1 illustrates the cyclic voltammograms of a 1000.0 µM isoproterenol obtained using the GQDs/SPE (Curve a) and an unmodified SPE (Curve b). As it can be easily noticed the maximum oxidation of isoproterenol occurs at 180 mV in the case of GQDs/SPE that is around 320 mV more negative than that observed in the case of the unmodified SPE.

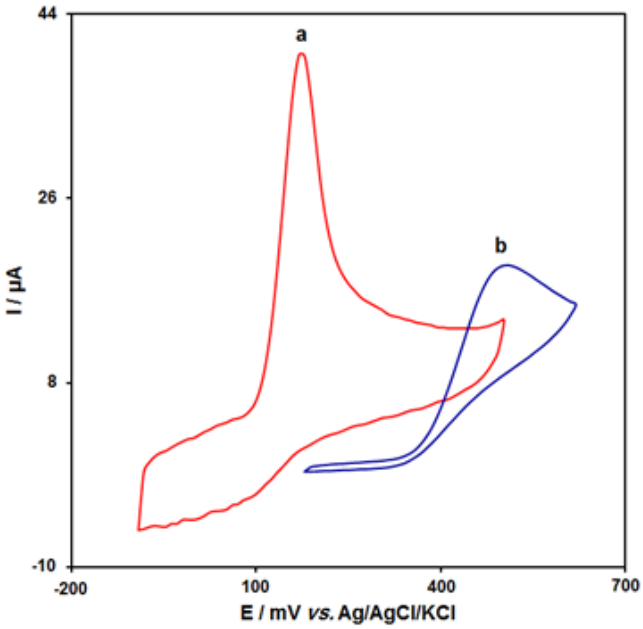

Fig. 1. Cyclic voltammograms of (a) GQDs/SPE and (b) bare SPE in0.1 M PBS (pH 7.0) in the presence of 1000.0 µM isoproterenol at the scan rate50 mVs^{-1}

3.2. Effect of scan rate on the results

Fig. 2 illustrates the effects of potential scan rates on the oxidation currents of isoproterenol, indicating that increasing the scan rate increased the peak currents. Also based on the fact that the plots of I_p against the square root of the potential scan rate ($v^{1/2}$) was linear, it was concluded that the oxidation process are is diffusion controlled.

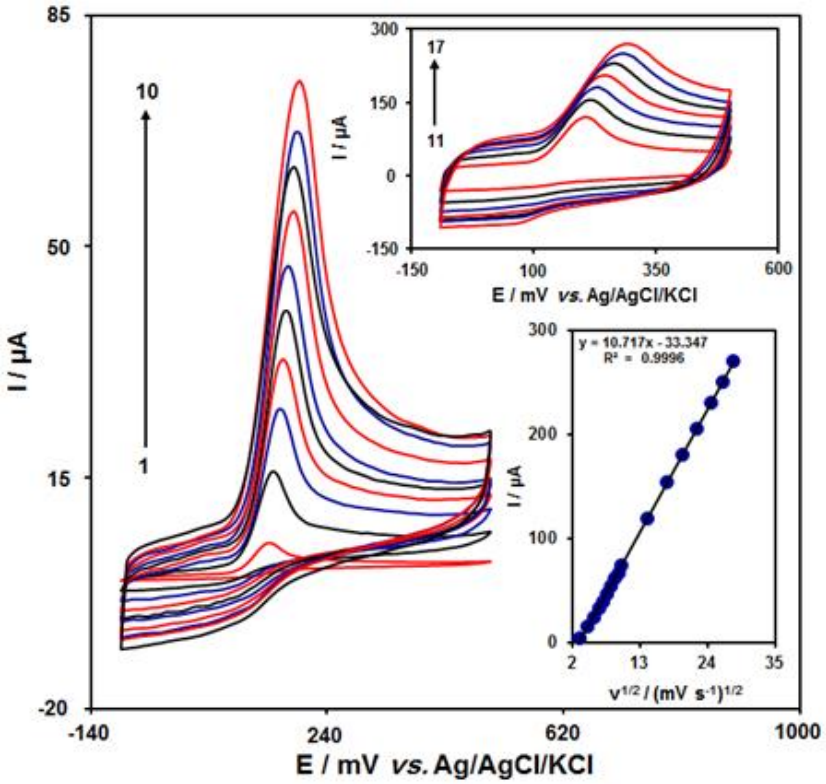

Fig. 2. Cyclic voltammograms of GQDs/SPEin 0.1 M PBS (pH 7.0) containing 1000.0 µM isoproterenol at various scan rates; numbers 1-17 correspond to 10, 20, 30, 40,50, 60, 70, 80, 90, 100, 200, 300, 400, 500, 600, 700 and 800 mV s^{-1}, respectively. Inset: variation of anodic peak current *vs*. $v^{1/2}$

3.3. Chronoamperometric analyses

The chronoamperometric analyses of the isoproterenol samples using the GQDs/SPE were performed at 0.2 V *vs*. Ag/AgCl/KCl (3.0 M) and the results obtained for the different isoproterenol samples in PBS (pH 7.0) are illustrated in Fig. 3. For chronoamperometric analysis of electroactive materials under mass transfer limited conditions, the Cottrell equation [48]:

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2}$$

Where D is the diffusion coefficient (cm^2 s^{-1}), and C_b is the bulk concentration (mol cm^{-3}), applies. Experimental plots of *I vs.* $t^{-1/2}$ were employed, with the best fits for different concentrations of isoproterenol (Fig. 3A). The slopes of the resulting straight lines were then plotted *vs.* isoproterenol concentration (Fig. 3B). From the resulting slope and Cottrell equation the mean value of the D was found to be 7.3×10^{-6} cm^2/s.

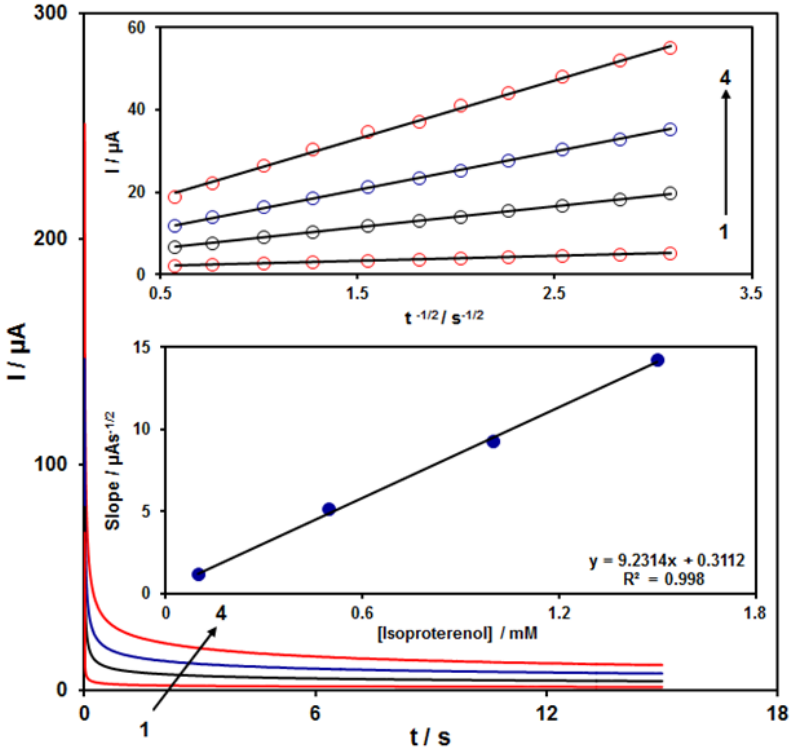

Fig. 3. Chronoamperograms obtained at GQDs/SPEin 0.1 M PBS (pH 7.0) for different concentrations of isoproterenol. The numbers 1–4 correspond to 0.1, 0.5, 1.0, and 2.0 mM of isoproterenol. Insets: (A) Plots of I *vs.* $t^{-1/2}$ obtained from chronoamperograms 1–4; (B) Plot of the slope of the straight lines against isoproterenol concentration

3.4. Calibration curves

The peak currents obtained for isoproterenol using the GQDs/SPE were used for the quantitative analysis of isoproterenol in water solutions. Given the advantage of DPV in terms of improved sensitivity and better characteristics for analytical applications, the modified electrode was used as the working electrode in DPV analyses in a range of isoproterenol solutions in 0.1 M PBS and the results (Fig. 4), show that there is a linear relation between the peak currents and concentrations of isoproterenol over the concentration range of 1.0-900.0 µM (with a correlation coefficient of 0.9993) and a detection limit (3σ) of 0.6 µM was obtained. These values are comparable with values reported by other research groups for electro- oxidation isoproterenol at the surface of chemically modified electrodes (see Table 1).

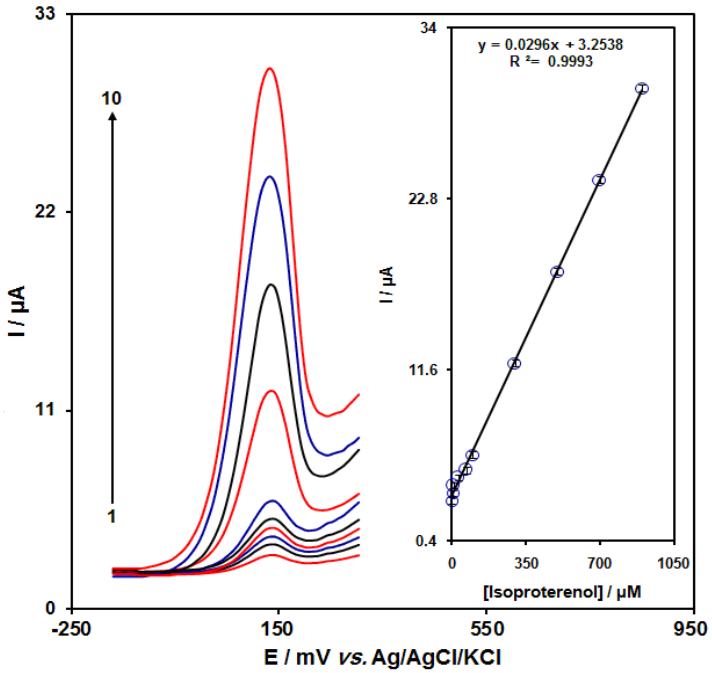

Fig. 4. DPVs of GQDs/SPE in 0.1 M (pH 7.0) containing different concentrations of isoproterenol. Numbers 1–10 correspond to1.0, 5.0, 10.0, 30.0, 70.0, 100.0, 300.0, 500.0, 700.0 and 900.0 µM of isoproterenol. Inset: plot of the electrocatalytic peak current as a function of isoproterenol concentration in the range of 1.0-900.0 µM

Table 1. Comparison of some electrochemical procedures used in the determination of isoproterenol

Electrode	**Modifier**	**Linear range (µM)**	**Detection limit (µM)**	**Ref.**
Glassy carbon	Poly(1-methylpyrrole)-DNA	2.0-60.0	0.16	[49]
Carbon paste	Ferrocenemonocarboxylic acid/Multiwall Carbon Nanotube	0.5-50.0	0.2	[50]
Carbon paste	Pyrogallol red/Multiwall Carbon Nanotube	0.8-570.0	0.47	[51]
Carbon paste	5-amino-3′,4′-dimethyl-biphenyl-2-ol/carbon nanotube	0.4-900.0	0.2	[52]
Carbon paste	(E)-2-((2 Chlorophenylimino)methyl)benzene-1,4- diol (CD)/ titanium dioxide nanoparticles	0.5-1000.0	0.47	[53]
Glassy carbon	Gold nanoparticles (AuNPs) and 2-(2,3-dihydroxy phenyl) benzothiazole (DPB)	0.1-900.0	0.082	[54]
Screen printed	Graphene quantum dots	1.0 - 900.0	0.6	This Work

3.5. Analysis of real samples

To assess the applicability of the application of the modified electrode for the determination of isoproterenol in real samples, the described method was applied to the determination of isoproterenol in isoproterenol ampoule and urine samples. For the purpose of this analysis the standard addition method was used and the results are given in Table 2. The observed recoveries of isoproterenol were satisfactory and the reproducibility of the results were demonstrated based on the mean relative standard deviation (R.S.D.).

Table 2. The application of GQDs/SPE for determination of isoproterenol in isoproterenol ampoule and urine samples. All concentrations are in μM

Sample	Spiked	Found	Recovery (%)	R.S.D. (%)
Isoproterenol ampoule	0	5.0	-	3.2
	2.5	7.4	98.7	2.4
	7.5	12.6	100.8	1.7
	12.5	18.1	103.4	2.3
	17.5	22.3	99.1	2.9
Urine	0	-	-	-
	5.0	5.1	102.0	3.4
	10.0	9.9	99.0	2.9
	15.0	14.7	98.0	1.9
	20.0	20.6	103.0	2.4

4. CONCLUSION

In the present study, we have proposed a screen printed electrode modified with graphene quantum dots (GQDs/SPE). This electrode has shown very good activity towards the generation of electrochemical oxidation signal of isoproterenol. The peak currents followed good linear correlation with the concentration of isoproterenol. The electrode has shown excellent sensitivity for isoproterenol signal. The detection limits in the case of isoproterenol was obtained as 0.6 μM. A simple way of modification has produced very good method of determination of isoproterenol; the method is suitable for real application.

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