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Highly Sensitive Determination of Theophylline Based on Graphene Quantum Dots Modified Electrode

Mohammad Reza Ganjali[1,2,*], *Zahra Dourandish*[3], *Hadi Beitollahi*[4,*], *Somayeh Tajik*[5],
Leila Hajiaghababaei[6], *Bagher Larijani*[7]

[1] Center of Excellence in Electrochemistry, School of Chemistry, College of Science, University of Tehran, Tehran, Iran
[2] Biosensor Research Center, Endocrinology & Metabolism Molecular-Cellular Sciences Institute, Tehran University of Medical Sciences, Tehran, Iran
[3] Department of Chemistry, Graduate University of Advanced Technology, Kerman, Iran.
[4] Environment Department, Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, Kerman, Iran
[5]Bam University of Medical Sciences, Bam, Iran
[6] Department of Chemistry, Yadegar-e-Imam Khomeini (RAH) Shahre Rey Branch, Islamic Azad University, Tehran, Iran
[7] Endocrinology and Metabolism Research Center, Endocrinology and Metabolism Clinical Sciences Institute, Tehran University of Medical Sciences, Tehran, Iran
[*]E-mail: ganjali@khayam.ut.ac.ir, h.beitollahi@yahoo.com

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In this study we introduce a novel modification for the surface of screen-printed electrode (SPE) by graphene quantum dot (GQD) in order to be used in the determination and detection of theophylline. An uncomplicated technique was employed to stabilize GQD on screen-printed electrode. Function evaluation of the GQD modified SPE (GQD/SPE) by cyclic voltammetry revealed enhanced electroactivity in the oxidation of theophylline in buffer solution of phosphate. Differential-pulse voltammetry (DPV), cyclic voltammetry (CV) and chronoamperometry were applied to determine the sensitivity of GQD/SPE toward detection of theophylline. A wide linear concentration range of 1.0–700.0 μM and detection limit of 0.2 μM (S/N = 3) obtained under optimized conditions. This sensor was successful in the assessment of theophylline in real samples.

Keywords: Theophylline, Graphite screen-printed electrode, Graphene quantum dots, Modified electrode

1. INTRODUCTION

Theophylline with IUPAC name of (1, 3-dimethyl-3,7-dihydro-1H-purin-2,6-dion), as a derivative of methyl xanthine is abundant in nature [1,2]. It is categorized as one of the important natural alkaloids which is found in large amounts in tea, coffee, and cocoa beans [3]. One of the mechanisms of theophylline action is through the approximately equal antagonization of adenosine (A1, A2 and A3) receptors [4]. In fact, it plays the role of a nonselective antagonist for adenosine receptor. Theophylline is effective in the treatment of respiratory diseases and prescribed in the therapy of asthma and chronic obstructive pulmonary disorder in adults. It has been also found that it is respiratory stimulators which can be advantageous in the therapy of infant apnea and acute asthmatic in children [5-8]. Its effective dose for bronchodilation in adult's blood plasma is 5–20 µg mL^{-1}. The therapeutic window of theophylline is narrow. Thus, the monitoring of its level in serum is essential to prevent toxicity. In cases of toxicity in higher doses, increased heart rate, diarrhea, anxiety, restlessness, dizziness, and even seizure can occur [9]. Low solubility of theophylline which confines its therapeutic effectiveness is increased by formation of its salts by inorganic acids (e.g. with hydrochloric acid). In addition, the inorganic ingredient can improve the hydrogen bonding interactions and the solid packing. In comparison with parent drug molecule, their corresponding salts have more chemical stability which facilitates the complex pathway in the drug development [10, 12]. Accordingly, detection of theophylline via an uncomplicated and reliable technique is highly desirable. Until now, numerous analytical methods were employed to detect and determine the theophylline featuring thin layer chromatography, gas chromatography-mass spectrometry, capillary electrophoresis, spectrophotometry and high-performance liquid chromatography [13-19]. However, the electrochemical methods are far more attractive due to their high sensitivity, good stability, inexpensive and easy to use equipment, and quick in response [20-33]. In this method of analysis, the challenging stage is the modification of electrode by appropriate modifiers to enhance the efficiency of the electrochemical assay [34-42]. Recently, thanks to nanoscience and nanotechnology, the fabrications of chemically modified electrodes by nanomaterials have been widely developed.

Semiconductor materials have recently become attractive in the chemical modification of electrodes since they provide high surface area, excellent catalytic activity and high absorptivity [43-65]. Today, screen-printed carbon electrodes (SPCEs) are prevalent in electrochemical assessments. SPCEs have surpassed the conventional three-electrode analyzers due to their particular advantages such as small size, inexpensive, simple fabrication, fast response, disposable, portable and easy mass production [66-70].

Graphene quantum dots (GQDs) are fragments of graphene with size of less than 30 nm. GQDs are zero dimension materials combining the characteristics of both carbon dots (CDs) and graphene [71-74]. Presently, GQDs have become attractive in various fields due to the quantum confinement and edge effects which give rise to unique electronic, optoelectronic, photoelectric, enlarged surface and high conductive properties. Bearing such exceptional characteristics, GQDs are an excellent nominative for the manufacture of electrochemical sensors. In addition, GQDs present more expanded area in contact with analyte which leads to enhanced area of electrochemical active surface in interaction with electroactive analytes. Due to the importance of geometric surface area in electrochemistry, modification of different types of electrodes by GQDs is expected to increase the electrochemical reaction's rate [75-79].

In the present research, we benefit from the advantages of GQDs in the modification of a screen printed electrode to study the electrochemical behavior of theophylline.

2. EXPERIMENTAL

2.1. Chemicals and Apparatus

TensoreII FT-IR infrared spectrometer was used in transmission mode for recording the Fourier transform infrared (FT-IR) spectra between the ranges of 4000–400 cm^{-1} to determine the chemical nature of formed bonds. An Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands) was employed to perform the electrochemical experiments and the system was controlled using a general purpose electrochemical system software.

The screen-printed electrode (DropSens, DRP-110, Spain) consists of three conventional electrodes: graphite counter electrode, a silver pseudo-reference electrode and an unmodified graphite working electrode. pH was measured by a Metrohm 710 pH meter.

Theophylline and all other reagents were analytical grade, and were purchased from Merck (Darmstadt, Germany). For the preparation of buffers, the orthophosphoric acid and its salts were used to provide the pH range of 2.0–9.0.

2.2. Synthesis of graphene quantum dots

Graphene quantum dots were prepared by direct pyrolysis of citric acid. In a typical synthesis procedure, a ceramic crucible containing 2 g citric acid monohydrate was heated to 250 °C in a muffle furnace. After 35 min, the furnace was turned off and gradually cooled down to room temperature. In crucible, the brown GQDs powders were prepared.

2.3. Preparation of the electrode

The bare screen-printed electrode was coated with GQDs according to the following simple procedure. 1 mg GQDs was dispersed in 1 mL aqueous solution within 45 min ultrasonication. Then, 5 µl of the prepared suspension was dropped on the surface of carbon working electrodes. It remains at room temperature until becomes dry.

2.4. Preparation of real samples

The theophylline oral solution was diluted by dilution factor of 500 with deionized water. Then, different volumes of the diluted solution was transferred into a 25 mL volumetric flask and diluted by PBS (pH 7.0) to the mark. Analysis the amount of theophylline in each sample was carried out 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 2,000 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 amount of theophylline. The theophylline content was analysed by the proposed method by using the standard addition method.

3. RESULT AND DISCUSSION

3.1. FT-IR Characterization

Fig 1 shows the FT-IR spectrum of GQDs. The absorption peaks of carboxyl and hydroxyl groups demonstrate the formation of GQDs and the presence of –COOH groups in nanomaterial. In the FT-IR spectrum, the peaks of C-O and the stretching vibration of C=O corresponding to carboxyl group appeared at 1279 and 1767 cm^{-1}, respectively [80].

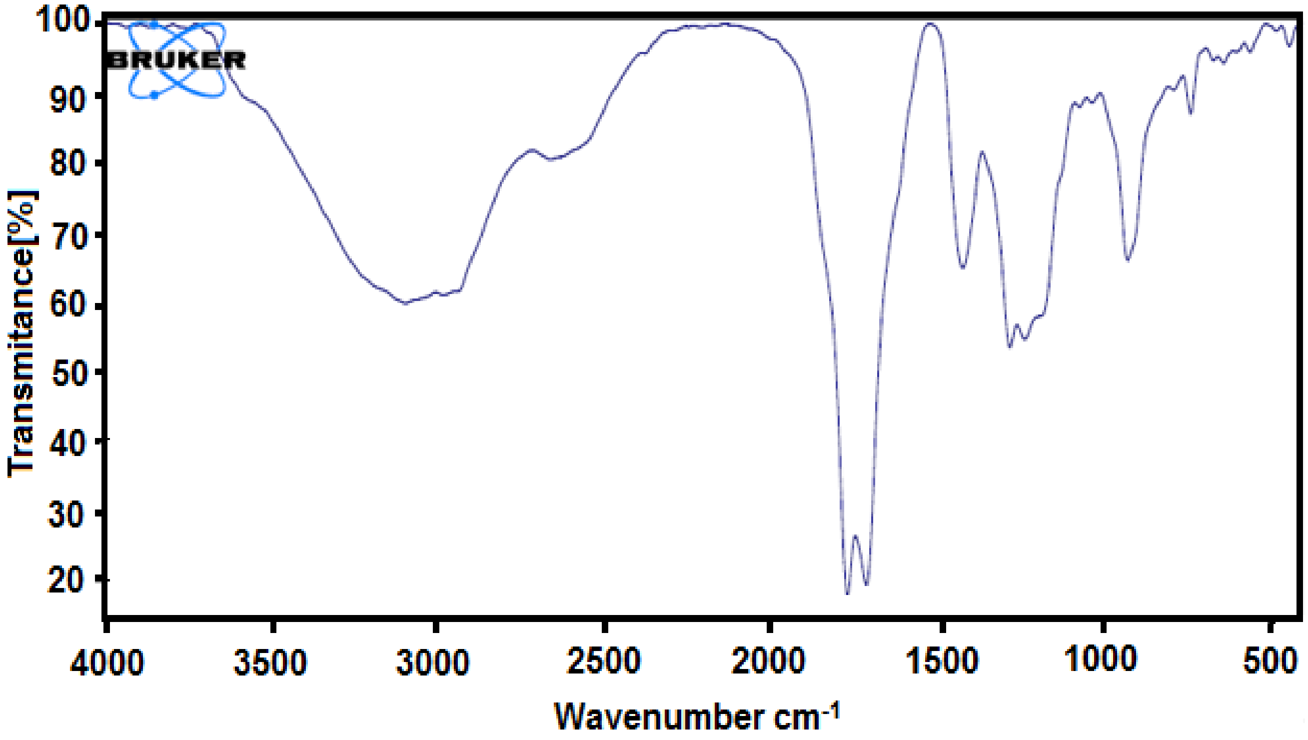


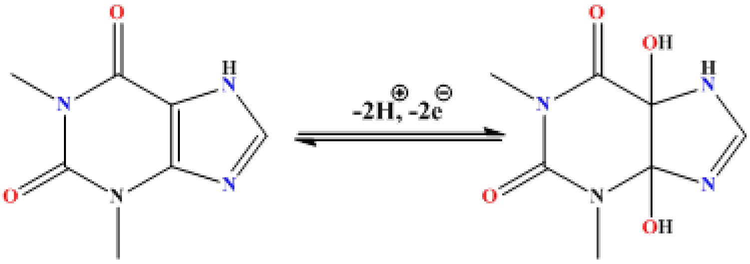
Figure 1. FT-IR spectrum of GQDs

The characteristic absorption peak at 1421 cm^{-1} is attributed to stretching mode of C=C bond. Another important peak in the FT-IR spectrum of GQDs is the stretching vibration of the H-bonding related to –OH group which appears as a broad absorption band around 3096 cm^{-1} [81,82].

3.2. Electrochemical profile of the analytes on the GQD/SPE

To study the electrochemical redox behaviour of theophylline which is a pH-dependent reaction (Scheme 1), it is necessary to obtain the optimized pH value in order to achieve the accurate results [83]. By performing the experiments by use of modified electrodes at various pH values ranging from 2.0–9.0, it was revealed that the best results for electro-oxidation of theophylline occur at pH=7.

The obtained cyclic voltammograms in the presence of 300.0 µM theophylline using the GQDs/SPE (Curve a) and bare SPE (Curve b) are shown in Fig. 2. According to CV results the maximum oxidation of theophylline on the GQDs/SPE occurs at 800 mV which is about 200 mV more negative compared with unmodified SPE.



Scheme 1. Oxidation of theophylline at modified electrode [83]

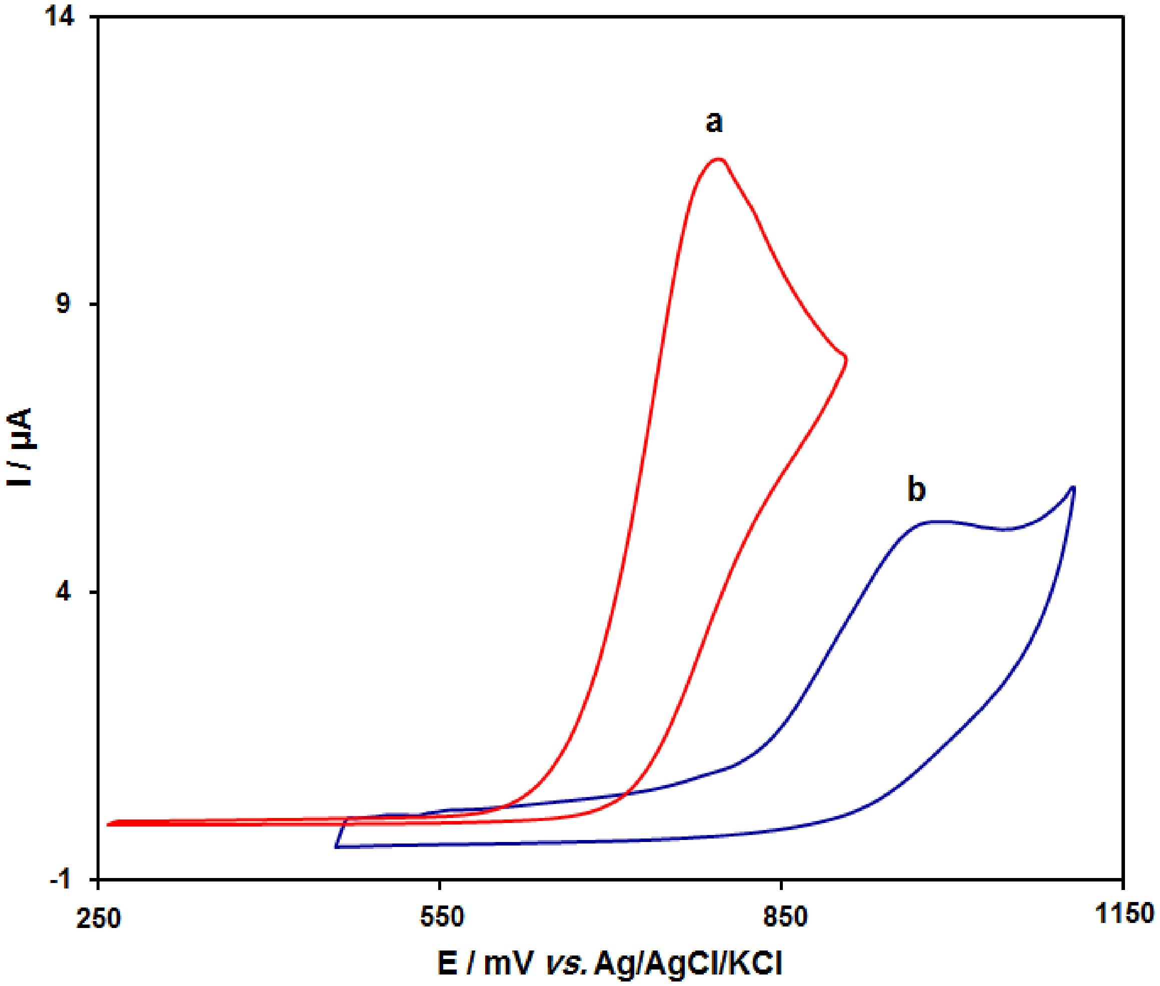


Figure 2. Cyclic voltammograms of (a) GQDs/SPE and (b) bare SPE in 0.1 M PBS (pH 7.0) in the presence of 300.0 µM theophylline at the scan rate 50 mVs^{-1}.

3.2. Effect of scan rate on the results

Increasing in scan rate leads to enhanced oxidation peak current according to the obtained results from the study of the effect of potential scan rates on the oxidation currents of theophylline, Fig. 3. In addition, there is a linear relationship between I_p and the square root of the potential scan rate ($\nu^{1/2}$) that demonstrates that the oxidation procedure of analyst is in control of diffusion.

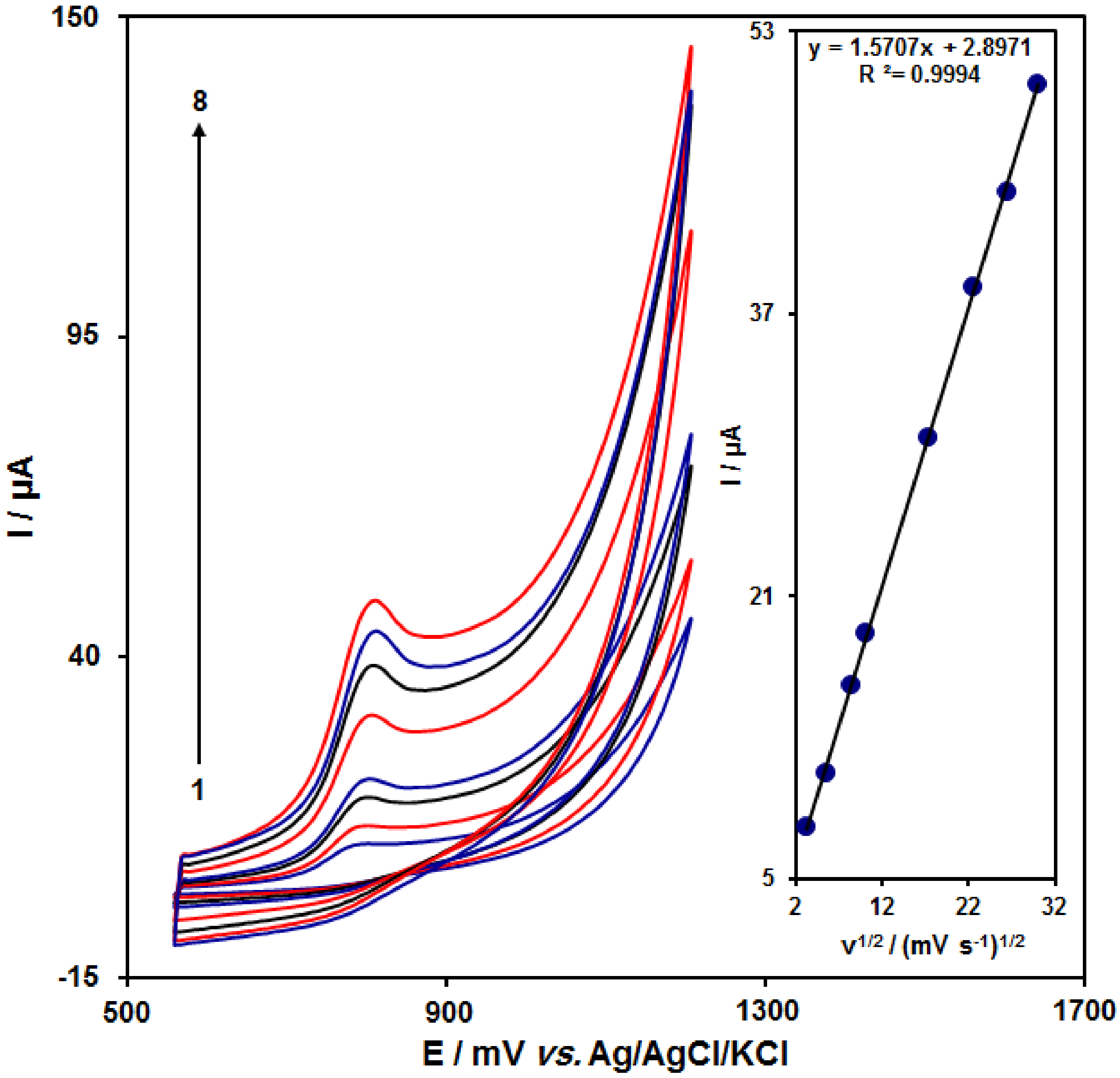


Figure 3. Cyclic voltammograms of GQDs/SPE in 0.1 M PBS (pH 7.0) containing 400.0 µM theophylline at various scan rates; numbers 1-8 correspond to 10, 30, 70, 100, 300, 500, 700 and 900 mV s^{-1}, respectively. Inset: variation of anodic peak current vs. $\nu^{1/2}$.

The Tafel curve of analyte was plotted applying the data from the rising sections (i.e. the Tafel regions) of the current–voltage curve obtained at 10 mVs^{-1} (Fig. 4). The kinetics of electron transfer in the electrode reactions, influence on the Tafel regions of the current potential curve. The Tafel slope was obtained 0.146 V implying to an electron rate determining step (RDS) in the electrode process with charge transfer coefficient (α) of 0.6 [84].

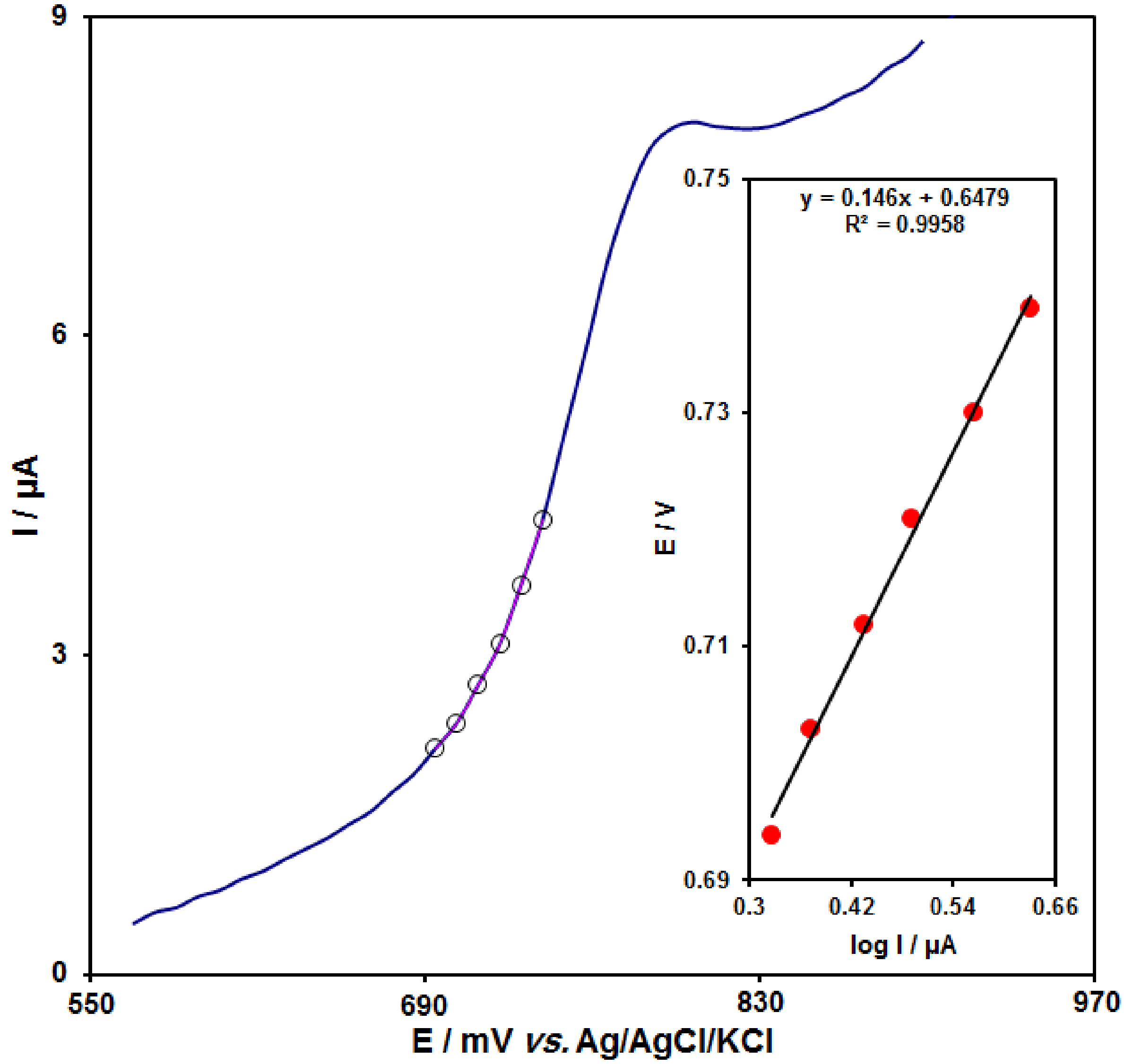


Figure 4. LSV (at 10 mV s^{-1}) of electrode in 0.1 M PBS (pH 7.0) containing 200.0 µM theophylline. The points are the data used in the Tafel plot. The inset shows the Tafel plot derived from the LSV.

3.3. Chronoamperometric analysis

The analysis of chronoamperometry for theophylline samples was performed by use of GQDs/SPE vs. Ag/AgCl/KCl (3.0 M) at 0.85 V. The Chronoamperometric results of different concentration of theophylline sample in PBS (pH 7.0) are demonstrated in Fig. 5.

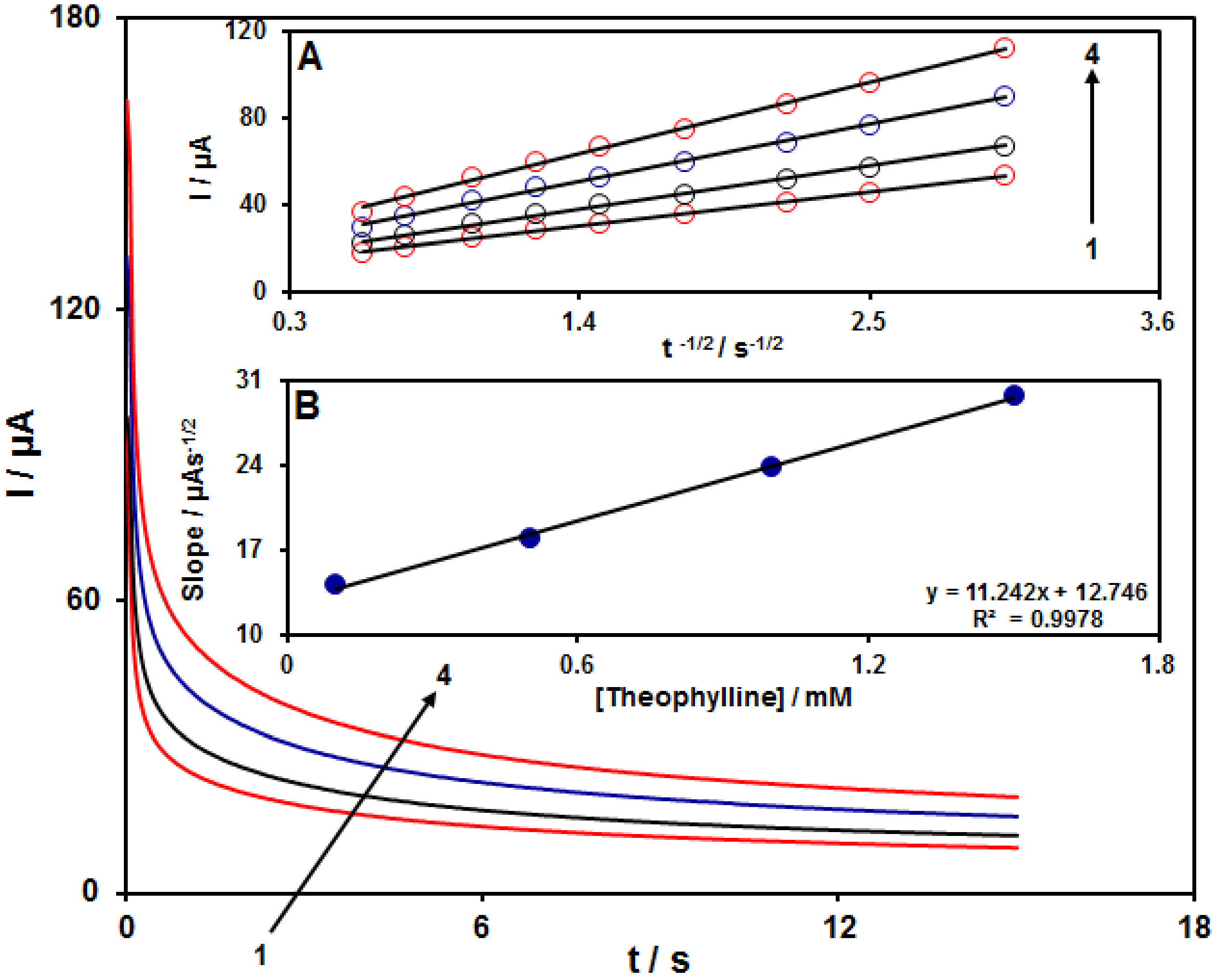


Figure 5. Chronoamperograms obtained at GQDs/SPE in 0.1 M PBS (pH 7.0) for different concentration of theophylline. The numbers 1–4 correspond to 0.1, 0.5, 1.0, and 1.5 mM of theophylline. Insets: (A) Plots of I *vs.* $t^{-1/2}$ obtained from chronoamperograms 1–4. (B) Plot of the slope of the straight lines against theophylline concentration.

The Cottrell equation for chronoamperometric analysis of electroactive moieties under mass transfer limited conditions is as follow [84]:

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

Where D represents the diffusion coefficient ($cm^2\ s^{-1}$), and C_b is the applied bulk concentration ($mol\ cm^{-3}$). Experimental results of I vs. $t^{-1/2}$ were plotted in Fig. 5A, with the best fits for different concentrations of theophylline. The resulted slopes corresponding to straight lines in Fig. 5A, were then plotted against the concentration of theophylline (Fig. 5B). The mean value of D was determined to be $1.1 \times 10^{-6}\ cm^2/s$ according to the resulting slope and Cottrell equation.

3.4. Calibration curves

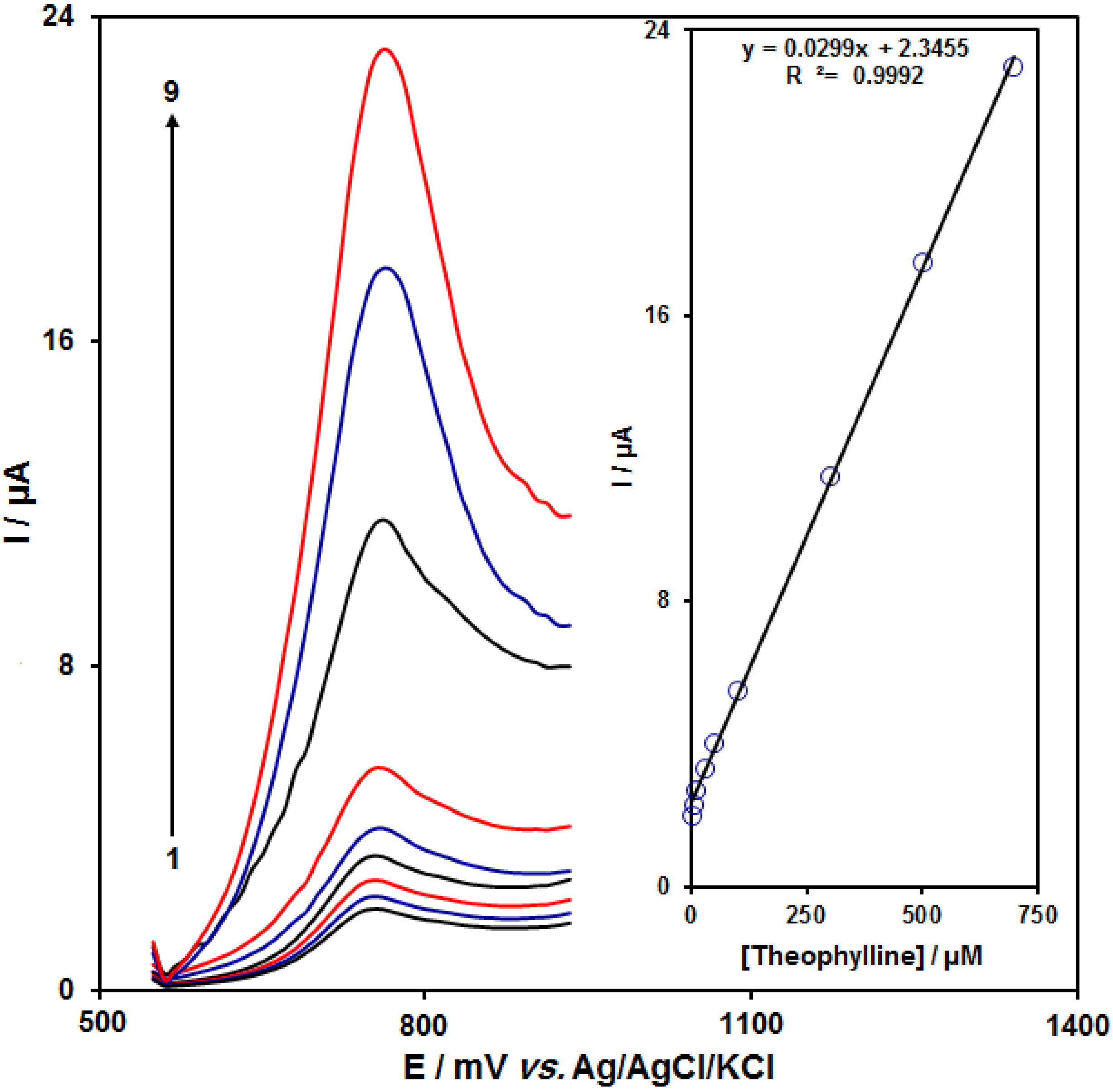


Figure 6. DPVs of GQDs/SPE in 0.1 M (pH 7.0) containing different concentrations of theophylline. Numbers 1–9 correspond to 1.0, 5.0, 10.0, 30.0, 50.0, 100.0, 300.0, 500.0 and 700.0 µM of theophylline. Inset: plot of the electrocatalytic peak current as a function of theophylline concentration in the range of 1.0-700.0 µM.

Based on the resulting peak currents of theophylline by use of GQDs/SPE, the quantitative analysis of theophylline was done in water solutions. The modified electrode (GQDs/SPE) as working electrode in the range of theophylline concentration in 0.1 M PBS was used in differential pulse voltammetry (DPV) due to the advantages of DPV including the improved sensitivity and better performance in analytical applications. According to the results, a linear relationship exists between the peak currents and concentrations of theophylline within the concentration range of 1.0-700.0 µM with the correlation coefficient of 0.9992. The detection limit was obtained 0.2 µM.

The features of the proposed QGD-SPE was compared with the values of some in previous works for determination of theophylline by different methods [85-89]. Table 1 shows the comparison in terms of type of modifier, used methodology, linear dynamic range (DLR) and limit of detection (LOD).

Table 1. Comparison of the efficiency of some modified electrodes used in the electro-oxidation of theophylline.

Electrode	Modifier	Method	LDR (µM)	LOD (µM)	Ref.
Screen printed	MWNTs/Au/poly-L-lysine	Square wave voltammetry	10.0-200.0	2.0	[85]
Glassy carbon	MIP by 4-amino-5-hydroxy-2,7naphthalenedisulfonic acid	Amperometry	0.4-17.0	0.32	[86]
Glassy carbon	MWNTs /MnO_2 nanoparticles	Differential pulse voltammetry	0.1-20.0	0.01	[87]
Gold	MIP made by dopamine	Differential pulse voltammetry	0.2-160	0.1	[88]
Glassy carbon	Tungsten disulfide (WS_2) nano-flowers/silver nanoparticles (Ag NPs) composites	Differential pulse voltammetry	0.5-150.0	0.003	[89]
Screen printed	GQD	Differential pulse voltammetry	1.0-700.0	0.2	This work

As it can be seen in Table 1, using GQD as a modifier for the electrode provides a wide linear range and acceptable LOD. It should be also noted that the type of modifier used in this work compared to other used modifiers, is a simple prepared ones.

3.5. Analysis of real samples

The applicability of this modified electrode in the determination of real samples was assessed through the determination of theophylline in oral and urine samples using the described method. In order to perform this analysis, standard addition method was employed and the results are listed in Table 2. Accordingly, the results of theophylline recoveries are satisfactory and the reproducibility of the results is proved by the mean relative standard deviation (R.S.D.).

Table 1. The application of GQD/SPE for determination of theophylline in theophylline oral solution and urine samples (n=5). All concentrations are in µM.

Sample	Spiked	Found	Recovery (%)	R.S.D. (%)
Theophylline oral solution	0	7.0	-	3.3
	5.0	12.1	100.8	1.9
	10.0	16.5	97.1	2.4
Urine	0	-	-	-
	5.0	4.9	98.0	2.9
	10.0	10.1	101.0	2.1

4. CONCLUSION

The results of this study introduce a new voltammetric sensor based on GQD/SPE for the detection of theophylline with considerable sensitivity. Comparing with the previous reported sensors, GQD/SPE demonstrated outstanding features of broad wide linear range and low detection limit towards theophylline. The proposed modified sensor provides an appropriate analytical tool for the assay of theophylline in clinical diagnosis and pharmaceutical analysis.

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