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Graphene quantum dots/ionic liquid-Modified Carbon Paste Electrode-Based Sensor for Simultaneous voltammetric determination of norepinephrine and acetylcholine

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In this work, a highly effective voltammetric sensor fabricated for simultaneous analysis of norepinephrine and acetylcholine. The sensor was fabricated by the modification of carbon paste electrode with graphene quantum dots/ionic liquid (GQDs/IL/CPE). The electrochemical behavior of epinephrine on the modified electrode was studied using cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometry (CHA).The results indicate that the electrochemical responses are improved significantly with the use of the modified electrode. The calibration curve obtained by DPV, under the optimized conditions, showed linear range of 0.2–400.0 μM for norepinephrine (limit of detection 0.06 μM).The sensor was successfully used to detect the analytes in real samples.

Keywords: Voltammetric sensor, Norepinephrine, Acetylcholine, Graphene quantum dots, Ionic liquid, Carbon paste electrode

1. INTRODUCTION

Norepinephrine (NE) is an important catecholamine neurotransmitter in the mammalian central nervous system. Norepinephrine functions as a neurotransmitter, and it is synthesized in the human body from L-tyrosine and secreted by the medulla of the adrenal gland along with epinephrine. Norepinephrine is commonly used as a drug of choice as a vasoconstrictor, cardiac stimulator and bronchodilator. It exists in protonated form at physiological pH. It is used for treating myocardial infarction hypertension, bronchial asthma and organic heart disease. Extreme abnormalities of norepinephrine concentration levels may lead to the occurrence of many diseases such as ganglia neuroblastoma, ganglion neuronal,

paraganglioma and Parkinson' disease. Recent reports have indicated that norepinephrine enhances adhesion of human immune deficiency virus1 (HIV-1)-infected leukocytes to cardiac micro vascular endothelial cells and also accelerates HIV replication via protein kinase [1-8].

Acetylcholine (ACh) has been known as one kind of the most important neurotransmitters, which is involved in neurotransmission processes in both the peripheral and central nervous systems. ACh is produced from choline in the presence of choline acetyltransferase and acetyl-coenzyme A in the axon terminals of neurons. In the peripheral nervous system, ACh binds to acetylcholine receptors (AChR) and regulates muscle contraction where as in the central nervous system, it plays a crucial role in the processes related to behavioral activities, arousal, attention, learning and memory. Abnormal levels of ACh are associated with nerve disorders including Parkinson's disease, Alzheimer's disease, progressive dementia, Schizophrenia and motor dysfunction [9-15].

In order to understand the functional and physiological aspects of neural disorders caused by abnormal in norepinephrine and acetylcholine concentrations, a sensitive, rapid and accurate detection tool is utmost required in clinical applications.

Various methods had been reported for norepinephrine and acetylcholine detection which includes high performance liquid chromatography [16, 17] gas chromatography mass spectrometry [18, 19] and electrochemical sensors [20, 21].

Among these methods, electrochemical method has attracted much attention because of its favorable properties of fast detection, low cost, portable, easy operation, high selectivity, and sensitivity and high efficiency, etc [22-44]. Yet the instantaneous detection of norepinephrine and acetylcholine is often masked due to extended overlapping voltammetric signal at bare electrodes and the overlapping of the oxidation voltammetric peaks makes the simultaneous determination vastly difficult. More recently, chemically modified electrodes (CMEs) have attracted much interest in the electrocatalytic oxidation/reduction of important redox systems. The operation mechanism of such electrodes depends on the properties of the modified materials used to promote selectivity and sensitivity toward the target analytes. This kind of electrode is inexpensive and possesses many advantages such as low background current, wide range of potential windows (in both cathodic and anodic region), easy fabrication, and rapid surface renewal. One of the most important properties of CMEs has been their ability to catalyze the electrode process via significant decrease of the overpotential and increase of the electron transfer kinetics with respect to the unmodified electrode [45-49].

Carbon paste electrodes (CPEs) are widely utilized to perform the electrochemical determinations of a variety of species owing to their low residual current and noise, ease of fabrication, wide anodic and cathodic potential ranges, renewability, and low cost [50-56].

Nanomaterials offer certain unique and specific electroanalysis properties that are only found in nanoscale materials. These properties derive from the enhanced diffusion of the target analyte based on convergent rather than linear diffusion, together with a high surface area, enhanced selectivity, catalytic activity, and a high signal-tonoise ratio. Convergent mass transport to the nanoelectrodes can speed up electrochemical processes, enhance electrochemical signals, and reduce background noise [57-59].

Graphene quantum dots (GQDs) are zero-dimensional 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. They are a kind of fragments of graphene, thus not only have the excellent performance of graphene, such as

good biocompatibility, suitable conductivity, and low toxicity etc, and the GQDs also exhibit new phenomena due to quantum confinement and edge effects. Taking advantages of the electrochemical properties similar to those of graphene, GQDs are widely used as a kind of suitable electrode material, not only in fuel cells, supercapacitors and photovoltaic cells but also in the field of electrochemical sensors. However, their applications in the analytical field have not been explored until now. Due to their unique properties, sensors based on GQDs can achieve a high level of performance [60-64].

Therefore, in the present work, we describe the preparation of a carbon paste electrode modified with graphene quantum dots and ionic liquid (GQD/IL/CPE) and investigate its performance for the electrocatalytic determination of norepinephrine in aqueous solutions. We also evaluate the analytical performance of the modified electrode for quantification of norepinephrine in the presence of acetylcholine. Finally, the detection procedure was confirmed to analyze norepinephrine and acetylcholine in real samples.

2. EXPERIMENTAL

2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolabpotentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. A conventional three electrode cell was used at 25 ± 1 °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and GQDs/2CBF/IL/CPEwere used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was used for pH measurements. Norepinephrine, acetylcholine and all of the other reagents were of analytical grade and were obtained from Merck (Darmstadt, Germany). The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0-9.0. Graphene quantum dots were synthesized as reported previously [65].

2.2. Preparation of the electrode

GQDs/IL/CPEs were prepared by mixing 0.2 g of graphenequantom dots with 0.8 g graphite powder and approximately, ~0.8 mL of ionic liquids with a mortar and pestle. The paste was then packed into the end of a glass tube (ca. 3.4 mmi.d. and 15 cm long). A copper wire inserted into the carbon paste provided the electrical contact.

For comparison, ionic liquid/carbon paste electrode in the absence of graphene quantom dots (IL-CPE) consistent of ionic liquid and graphite powder, graphene quantom dots carbon paste electrode (GQDs-CPE) consistent of graphene quantom dots, graphite powder and paraffin oil, and bare carbon paste electrode (CPE) consistent of graphite powder and paraffin oil were also prepared in the same way.

2.3. Preparing real samples

Samples of urine have been kept in a refrigerator directly after gathering. Ten millilitres of samples have been centrifuged for fifteen minutes at 2,000 rpm. The supernatant has been filtered by a 0.45 µm filter. Next, various volumes of solution has been transported into a 25 millilitres volumetric flask and diluted to the mark with PBS (pH= 7.0). This diluted urine samples were anaesthetized with different amounts of norepinephrine and acetylcholine. Content of norepinephrine and acetylcholinehave been analyzed by the suggested procedure by employing the standard addition method.

One milliliter of norepinephrine from the ampoule was diluted to 10 mL with 0.1 M PBS (pH 7.0). Then, different volumes of the diluted solution were transferred into a series of 25 mL volumetric flasks and diluted to the mark with PBS. The norepinephrine and acetylcholine contents were determined by the proposed method using the standard addition method.

One milliliter of acetylcholine from the ampoule was diluted to 10 mL with 0.1 M PBS (pH 7.0). Then, different volumes of the diluted solution were transferred into a series of 25 mL volumetric flasks and diluted to the mark with PBS. The norepinephrine and acetylcholine contents determined by the proposed method using the standard addition method.

3. RESULTS AND DISCUSSION

3.1. Electrochemical properties of norepinephrineon GQDs/IL/CPEsurface

The electrochemical behavior of norepinephrine is dependent on the pH value of the aqueous solution. Therefore, pH optimization of the solution seems to be necessary in order to obtain the electrocatalytic oxidation ofnorepinephrine. Thus the electrochemical behavior of norepinephrine was studied in 0.1 M PBS in different pH values (2.0< pH<9.0) at the surface of by CV. It was found that the electrocatalytic oxidation of norepinephrine at the surface of GQDs/IL/CPE was more favored under neutral conditions than in acidic or basic medium. This appears as a gradual growth in the anodic peak current. Thus, the pH 7.0 was chosen as the optimum pH for electrocatalysis of norepinephrine oxidation at the surface of GQDs//IL/CPE.

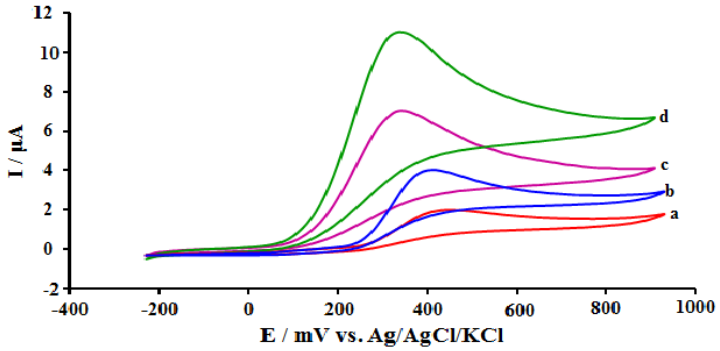

Figure 1. Cyclic voltammograms of a CPE, b GQDs -CPE, c IL-CPE, and d GQDs/IL/CPE in the presence of 100.0 µM mangiferin at a pH 7.0, respectively. In all cases the scan rate was 50 mV s^{-1}.

Fig. 1 displays cyclic voltammetric responses from the electrochemical oxidation of 100.0 µM norepinephrine at the surface of GQDs/IL/CPE (curve d), IL-CPE (curve c), GQDs –CPE (curve b), and bare CPE (curve a). The results showed that the oxidation of norepinephrine is very weak at the surface of the bare CPE, but in the presence of ILs in CPE could enhance the peak current and decrease the oxidation potential (decreasing the overpotential). A substantial negative shift of the currents starting from oxidation potential for norepinephrine and dramatic increase of the current indicates the catalytic ability of GQDs/IL/CPE (curve d) and IL-CPE (curve c) to norepinephrine oxidation.

The results showed that the combination of G and the ionic liquid (curve d) definitely improved the characteristics of norepinephrine oxidation. However, GQDs/IL/CPE shows much higher anodic peak current for the oxidation of norepinephrine compared to IL-CPE, indicating that the combination of GQDs and IL has significantly improved the performance of the electrode toward norepinephrine oxidation.

3.2. Effect of scan rate on the results

Researchers investigated the impact of the rates of potential scan on norepinephrine oxidation current (Figure 2A).

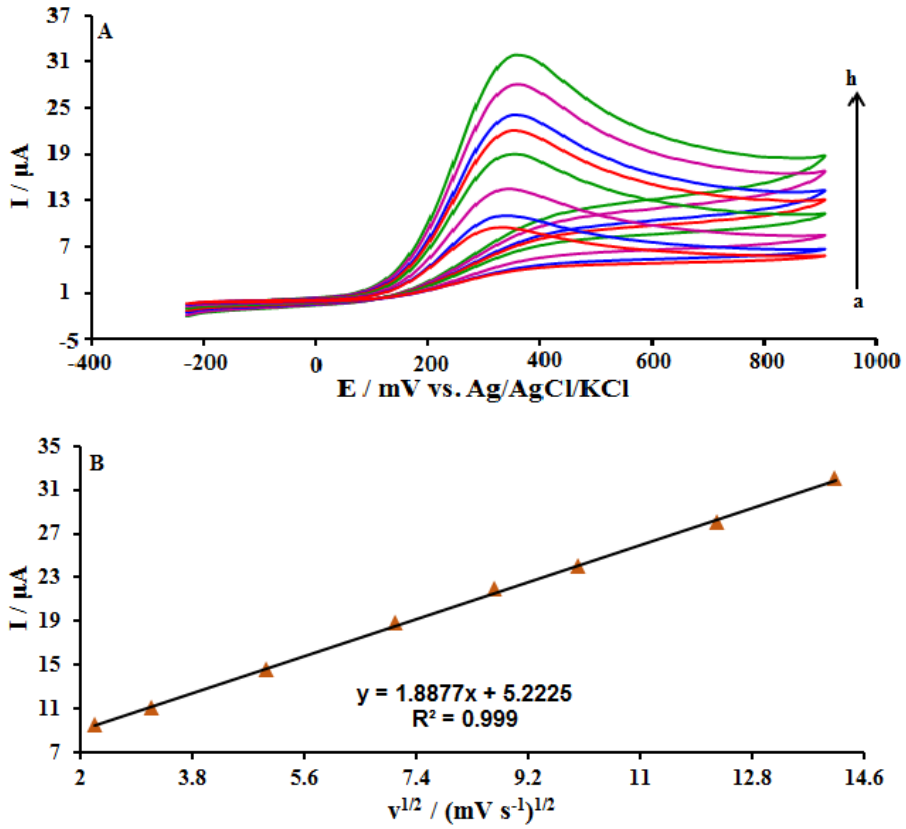

Figure 2.(A) Cyclic voltammogramsof GQDs/IL/CPE in 0.1 M PBS (pH 7.0) containing 150.0 µM of norepinephrinevarious scan rates. The indexes a-h correspond to 5, 10, 25, 50, 75, 100, 150 and 200 mV s^{-1}. (B) variation of anodic peak current with square root of scan rate.

Findings indicated induction of enhancement in the current of the peak by the increased potential scan rate. Additionally, diffusion in oxidation processes are monitored, as inferred by the linear dependence of the anodic peak current (Ip) on the square root of the potential scan rate ($\nu^{1/2}$) (Figure 2B).

3.3. Chronoamperometric measurements

Chronoamperometric measurements of norepinephrine at GQDs/IL/CPEwere carried out by setting the working electrode potential at 0.38 V vs. Ag/AgCl/KCl (3.0 M) for the various concentrations of norepinephrine in 0.1 MPBS (pH 7.0) (Fig.3A).

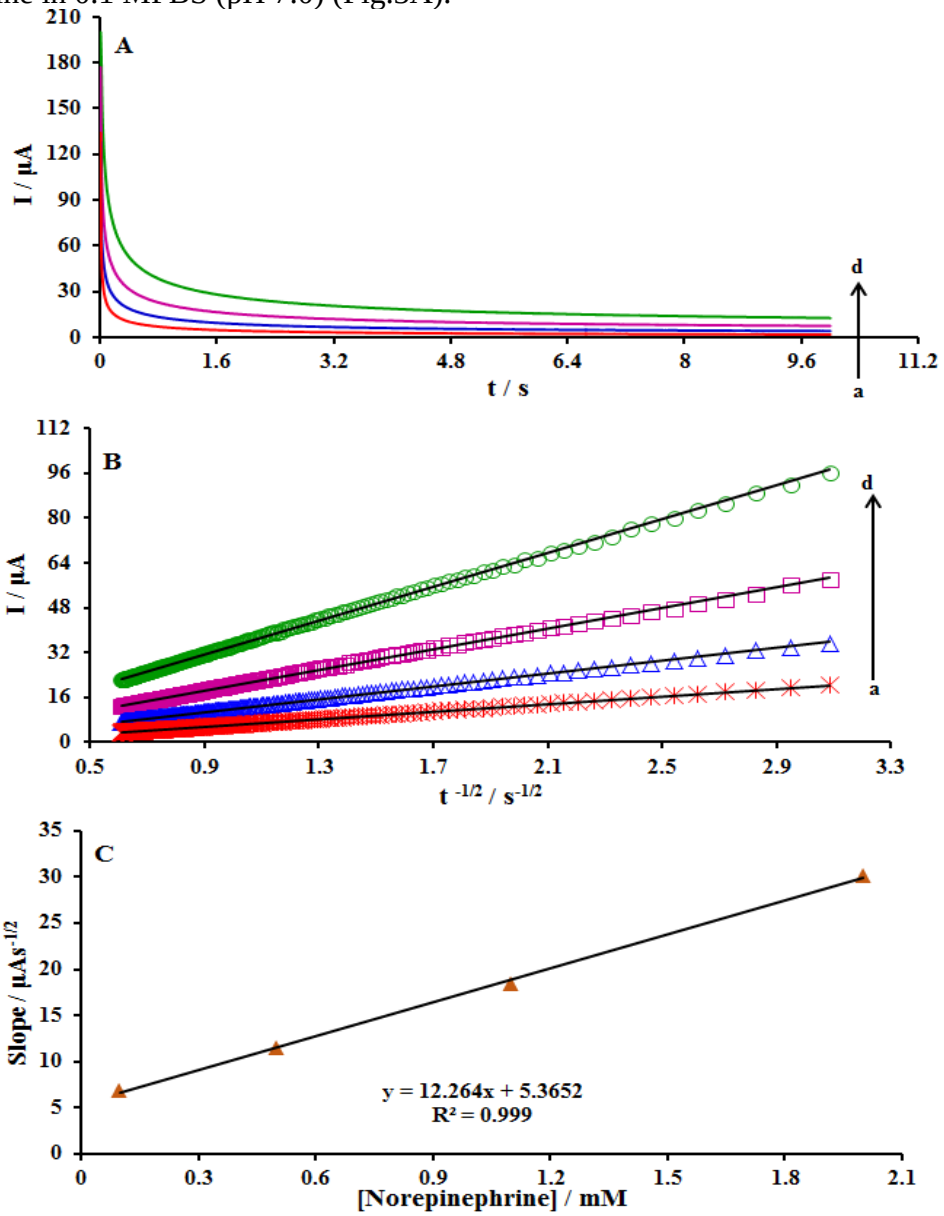

Figure 3.A) Chronoamperograms obtained at GQDs/IL/CPEin 0.1 M PBS (pH 7) for different concentration of norepinephrine. The indexes a-d correspond to 0.1, 0.5, 1.1 and 2.0 mM of norepinephrine. (B) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms a–d. (C) Plot of the slope of the straight lines against norepinephrine concentration.

For an electroactive material (norepinephrine 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 [66].

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

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 norepinephrine (Fig. 3B). The slopes of the resulting straight lines were then plotted vs. norepinephrineconcentration (Fig. 3C). From the resulting slope and Cottrell equation the mean value of the D was found to be $1.6\times10^{-6}cm^2/s$.

3.4. Calibration plot and limit of detection

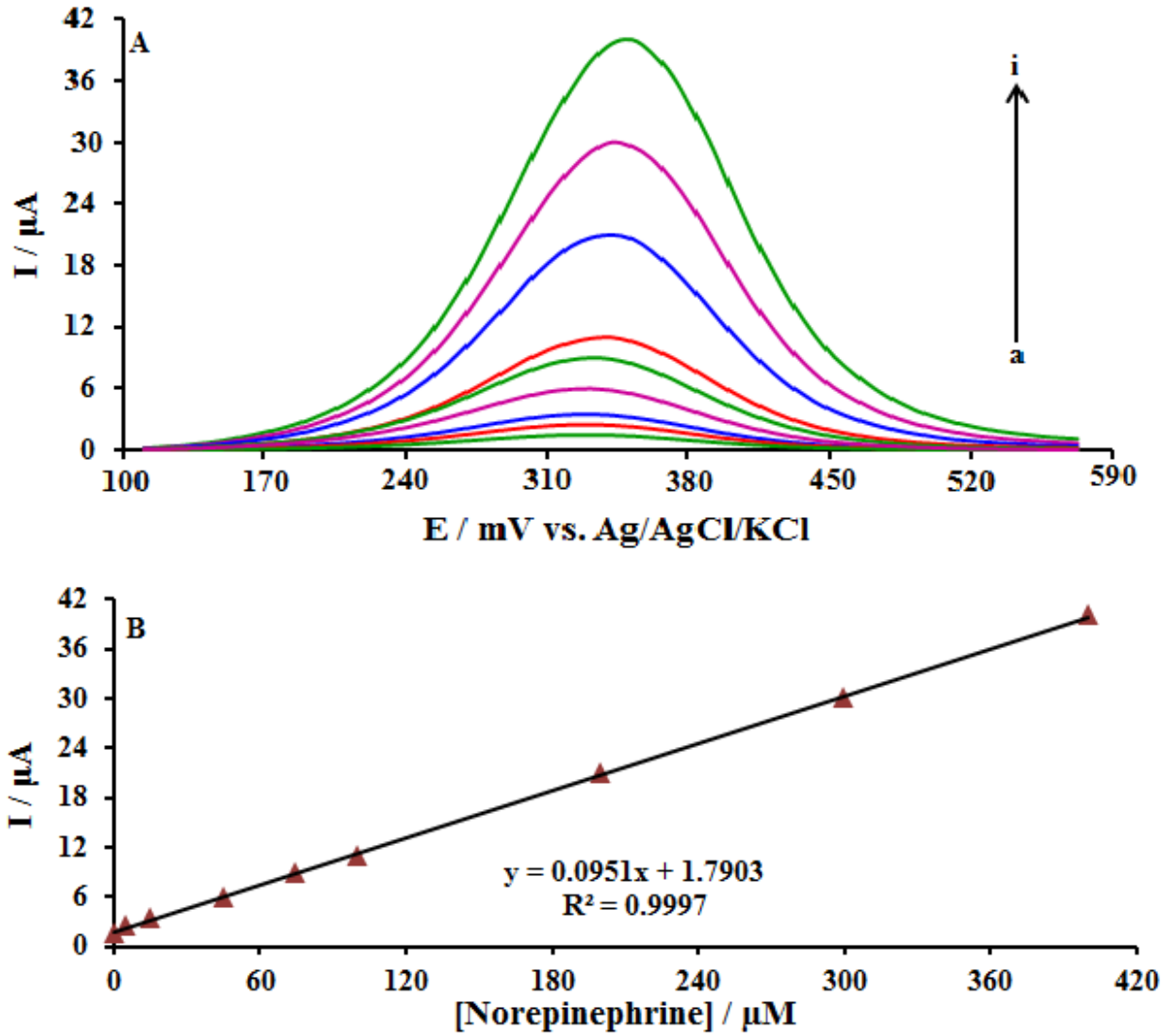

Figure 4.(A) Differential pulse voltammograms of GQDs/IL/CPEin 0.1 M PBS (pH 7.0) containing different concentrations of norepinephrine. The indexes a-I correspond to 0.2, 5.0, 15.0, 45.0, 75.0, 100.0, 200.0, 300.0 and 400.0 µM of norepinephrine. (B) The plot of the peak current as a function of norepinephrine concentration in the range of 0.2–400.0 µM.

The norepinephrinepeak currents via the GQDs/IL/CPEwere applied to quantitatively analyzenorepinephrine within water solutions. Due to the differential pulse voltammetry advantages concerning enhanced sensitivity and improved investigative utilization properties, the adjusted electrode was applied as a working electrode in DPV analysis within an norepinephrinerange solution in 0.1 M PBS (Fig. 4A).

In regard to Differential pulse voltammograms of norepinephrine via GQDs/IL/CPE, linear activity was evident within the 0.2-400.0 µM range and 0.9997 correlation coefficient (Fig. 4B). The relevant detection limit was 0.06 µM.These values are comparable with the valuesreported by other research groups for electrocatalytic oxidation of norepinephrineat the surface of chemically modified electrodes (see Table 1).

Table 1. Comparison of the efficiency of some electrodes used in detection of norepinephrine.

Electrode	Modifier	LDR (µM)	LOD (µM)	Ref.
Screen Printed	MWNTs-ZnO/chitosan composites	0.5–30.0	0.2	21
Carbon Paste	Poly (glutamic acid)	51.0–344.0	0.43	67
Glassy Carbon	Molecularly imprinted polymer-coated PdNPs	0.5–80.0	0.1	68
Glassy Carbon	Graphene quantum dots/gold nanoparticles	0.5-7.5	0.15	69
Carbon Paste	Graphene quantum dots/ionic liquid	0.2–400.0	0.06	This Work

3.5. Simultaneous Determination of norepinephrine and acetylcholine

We have not seen any report about using an CPE modified with GQDs//IL for determining norepinephrine and acetylcholine. Moreover, due to reality that electro-chemical detection of norepinephrine in the front of acetylcholinewith the help of un-modified electrodes has the caveat of interventions by acetylcholinebecause of relative adjacent oxidation capacities of the two specimens, it can be regarded a crucial phase. Such a phase has been conducted by simultaneous alterations of analytes concentrations and achieving Differential pulse voltammograms (Figure 5).

Findings reported certain anodic at 330 and 720 mV for norepinephrine and acetylcholineoxidation, proving using theGQDs/IL/CPE, these two analytes can be detected without severe interventions from each another (Figure 5).

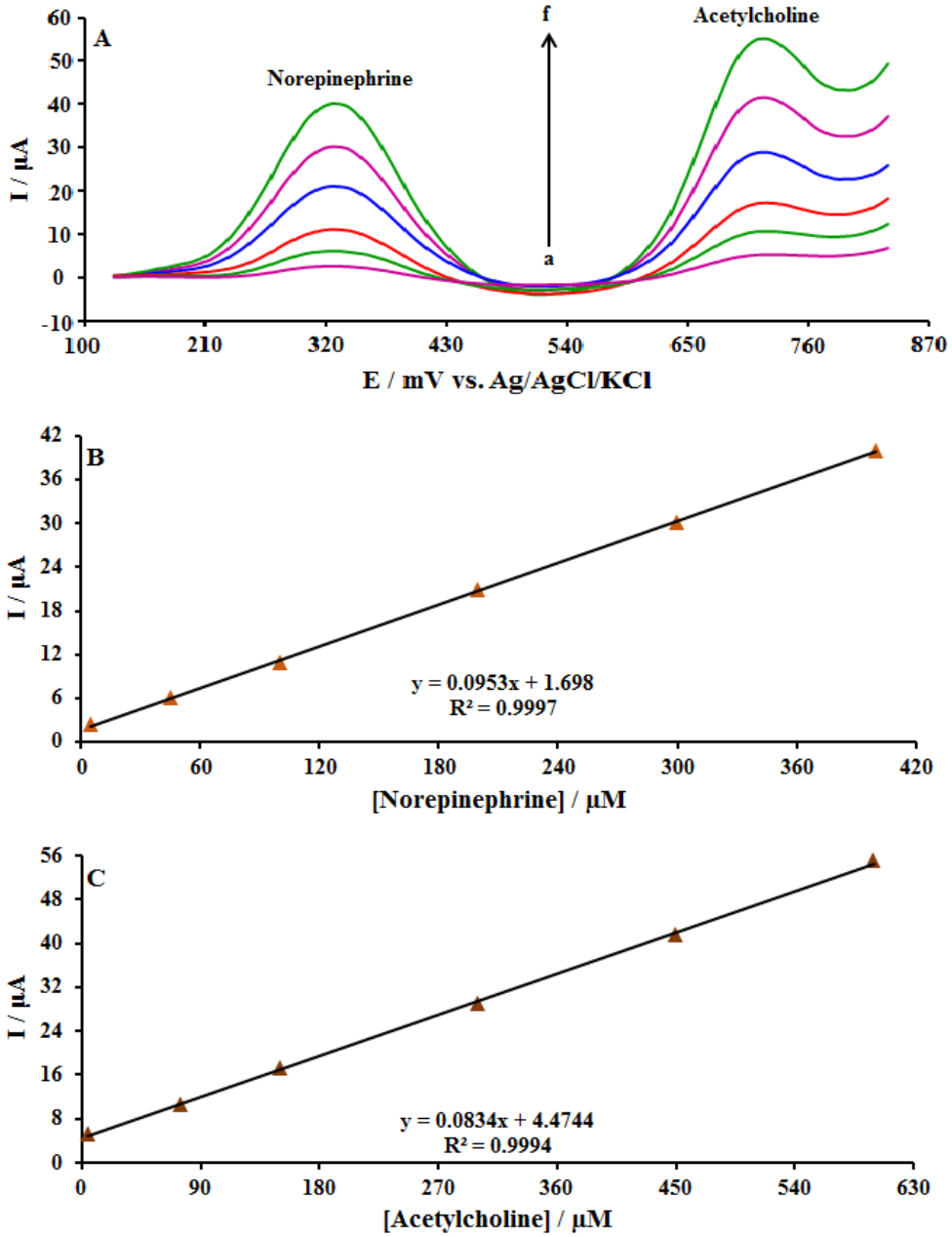

Figure 5.(A) Differential pulse voltammograms of GQDs/IL/CPEin 0.1 M PBS (pH=7.0) with various concentrations of norepinephrine+acetylcholine. The indexes a-f correspond to5.0+5.0, 45.0+75.0, 100.0+150.0, 200.0+300.0, 300.0+450.0 and 400.0+600.0µM of norepinephrine+acetylcholine, respectively. (B) plot of Ip versus norepinephrine concentrations, (C) plot of Ip versus acetylcholine concentrations.

3.6. Real sample analysis

In order to evaluate the analytical applicability of the proposed method, also it was applied to the determination of norepinephrine and acetylcholine in real samples. The results are listed in Table 2. Satisfactory recovery of the experimental results was found for norepinephrine and acetylcholine. The reproducibility of the method was demonstrated by the mean relative standard deviation (R.S.D.).

Table 2. The application of GQDs/IL/CPE for determination of norepinephrine and acetylcholine in real samples (n=5)

Sample	Spiked		Found		Recovery (%)		R.S.D. (%)	
	NE	ACH	NE	ACH	NE	ACH	NE	ACH
NE Ampoule	0	0	4.0	-	-	-	2.3	-
	2.5	5.0	6.4	5.1	98.5	102.0	3.4	1.8
	5.0	10.0	9.3	9.9	103.3	99.0	1.9	2.4
	7.5	15.0	11.2	15.2	97.4	101.3	2.6	3.3
	10.0	20.0	14.2	19.5	101.4	97.5	2.4	1.9
ACHAmpoule	0	0	-	3.0	-	-	-	3.4
	5.0	4.0	4.9	7.2	98.0	102.9	2.6	1.8
	10.0	6.0	10.3	8.9	103.0	98.9	3.5	2.4
	15.0	8.0	15.3	11.2	102.0	101.8	1.7	2.8
	20.0	10.0	19.6	13.1	98.0	100.8	2.5	2.6
Urine	0	0	-	-	-	-	-	-
	7.0	7.5	6.8	7.7	97.1	102.7	1.7	3.0
	12.0	12.5	12.3	12.4	102.5	99.2	3.2	2.0
	17.0	17.5	16.8	17.9	98.8	102.3	2.2	2.3
	22.0	22.5	22.2	22.3	100.9	99.1	2.6	2.7

4. CONCLUSIONS

In summary, a GQDs/IL/CPE was developed for the electrochemical simultaneous determination of norepinephrine and acetylcholine. The electrochemical behavior of norepinephrine was investigated at GQDs/IL/CPE by CV, DPV and CH in a phosphate buffer solution (pH 7.0). GQDs/IL/CPE as aelectrochemical sensor exhibited catalytic activity toward the oxidation of norepinephrine. The potential of norepinephrine oxidation was shifted to more negative potentials, and its oxidation peak current increased on the modified electrode. In addition, the GQDs/IL/CPE exhibits two separated oxidation signals for simultaneous analysis of norepinephrine and acetylcholine with $\Delta E\sim 390$ mV. The obtained results showed good linear relationship between the oxidation peak currents of norepinephrine and acetylcholine and their concentrations in the range 0.2 -400.0μM. Finally, GQDs/IL/CPE operates well in the determination of norepinephrine and acetylcholine in norepinephrine ampoule, acetylcholine ampoule and urine samples with good accuracy and precision.

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