

Electrochemical Determination of Adrenaline Using Voltammetric Sensor Employing NiO/CNTs Based Carbon Paste Electrode

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In the present study we tried for synthesis of NiO/CNTs nanocomposite and application of synthesized nanocomposite for fabrication of NiO/CNTs nanocomposite modified carbon paste electrode (CPE/NiO/CNTs) as highly square wave voltammetric sensors for determination of adrenaline. The NiO/CNTs was characterized with transmission electron microscopy (TEM) and x-ray powder diffraction (XRD) methods. The electro-oxidation signal of adrenaline showed an irreversible response at 0.3 V. The oxidation current of adrenaline improved ~2.0 times compared to carbon paste electrode. At the best electrochemical conditions, the voltammetric oxidation signal of adrenaline showed linear dynamic ranges (0.08-900.0 μM) with a detection limit of 0.01 μM . The CPE/NiO/CNTs has been found highly selective tool for the detection of adrenaline in ampule and urine samples.

Keywords: NiO/CNTs nanocomposite, Modified electrode, Adrenaline, Voltammetric determination

1. INTRODUCTION

Adrenaline or epinephrine released in the human body when persons feeling a strong emotion. Epinephrine is produced in adrenal glands and is necessary for nervous system. Also, the presence of adrenaline is essential to survive of human body, but it release from the body when person is under stress. Sudden numbness, slurred speech and worsened breathing trouble are important problems after overdose with adrenaline in human body. Therefore, analysis of adrenaline in human body and

pharmaceutical compounds are very important. Capillary electrophoresis [1], liquid chromatography [2, 3], flow injection analysis [4], electro-chemiluminescence [5], fluorimetry [6] and electrochemical methods [7–10] were suggested for determination of adrenaline in biological and pharmaceutical samples.

Application of electrochemical methods can be useful for analysis of electroactive compounds due to good sensitivity and low cost [11-25]. On the other hand, electrochemical systems can be converting to portable systems for in vivo and in vitro analysis.

Application of modified electrodes as working electrode in electrochemical systems is useful for trace level analysis. Modified electrodes reduce overvoltage of redox process and increasing sensitivity for electro-active compounds analysis [26-36].

Nano-materials are good choice for modification of electrodes due to high surface area and good electrical conductivity [37-45]. In between, metal based nanomaterials showed better electrical conductivity for fabrication of highly sensitive electrochemical sensor [46-50].

In this study, we synthesized NiO/CNTs nanocomposite by chemical precipitation method. In continuous, we used NiO/CNTs for modification of carbon paste electrode as an electrochemical sensor for determination of adrenaline in pharmaceutical samples. The CPE/NiO/CNTs showed high ability for analysis of adrenaline in real samples.

2. EXPERIMENTAL

2.1. Chemicals

Adrenaline, nickel (II) nitrate hexahydrate, sodium hydroxide and other chemicals were purchased from Merck.

A 1.0×10^{-2} M adrenaline solution was preparing by dissolving 0.183 g adrenaline in phosphate buffer solution (pH=8.0) in a 100-mL volumetric flask. Phosphate buffer 0.1 M solutions (PBS) with different pH values were used for optimization of pH.

2.2. Apparatus

Electrochemical investigations were performed by Autolab systems using Nova software. A electrochemical cell assembly consisting of a CPE/NiO/CNTs as a working electrode, platinum wire as a counter electrode and an Ag/AgCl/KCl_{sat} electrode as a reference electrode was used.

2.3. Synthesis NiO/CNTs

For synthesis of NiO/CNTs, 1.0 g functional single wall carbon nanotube (SWCNTS/COOH) dispersed in 50 mL 0.1 M sodium hydroxide and ultrasonicated for 30 min. The nickel (II) nitrate hexahydrate solution was added drop wise to previous solution. The precipitated Ni(OH)₂ were cleaned with deionized water and ethanol then calcined at 450 °C for 2.0 hours.

2.4. Preparation of CPE/NiO/CNTs

CPE/NiO/CNTs were prepared by mixing of 0.05 g of NiO/CNTs and 0.95 g graphite. Then the mixture was mixed well for 55 min by paraffin oil as a binder. A portion of the paste was filled firmly into one glass tube as described above to prepare CPE/NiO/CNTs.

2.5. Preparation of real samples

The ampoule sample was purchased from local pharmacy and use without any pretreatment.

10 mL of the urine was centrifuged for 35 min at 3000 rpm and filtered out using a 0.45 μm filter. The solution was transferred into the voltammetric cell to be analyzed by standard addition method.

3. RESULTS AND DISCUSSION

3.1. X-Ray diffraction of NiO/CNTs

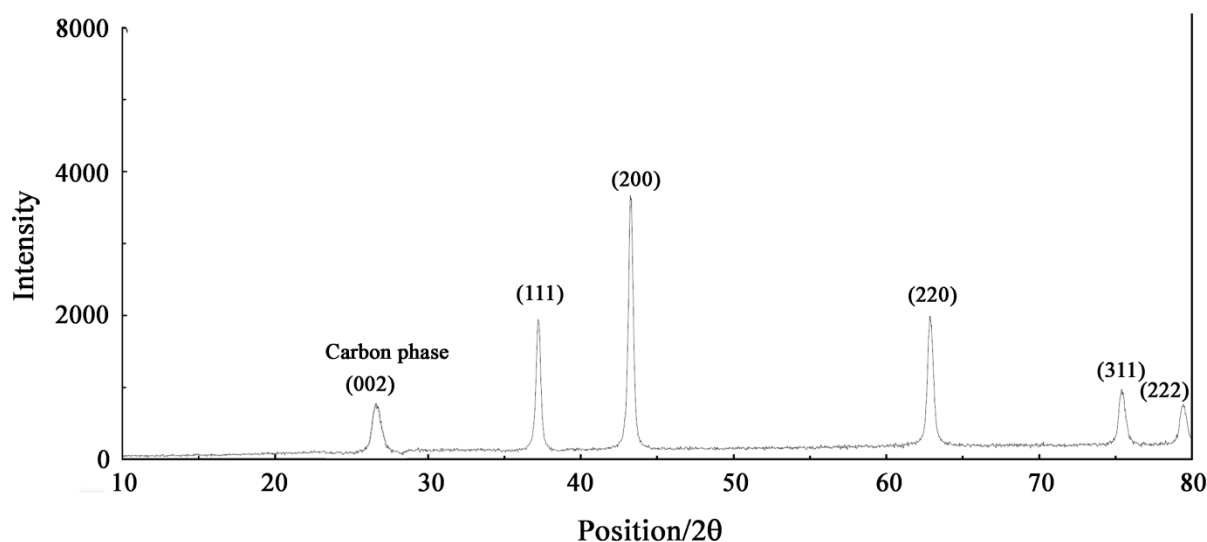


Figure 1. XRD patterns for NiO/CNTs synthesized in this work.

The NiO/CNTs nanocomposite was characterized with XRD method and the obtained data are presence in Fig. 1. The miller indexes for synthesized NiO nanoparticle are agreed with JCPDS No. 04-0835. Also, the presence of miller index bond (002) relative to single wall carbon nanotubes in $2\theta \sim 26^\circ$ confirm the synthesized of NiO nanoparticle at a surface of carbon nanotubes. The grain size of the NiO nanoparticle was obtained ~ 22 nm by Scherrer equation.

On the other hand, TEM technique was used for the morphological investigation of NiO/CNTs nanocomposite (Fig. 2). As can be seen, NiO nanoparticle loaded onto carbon nanotubes.

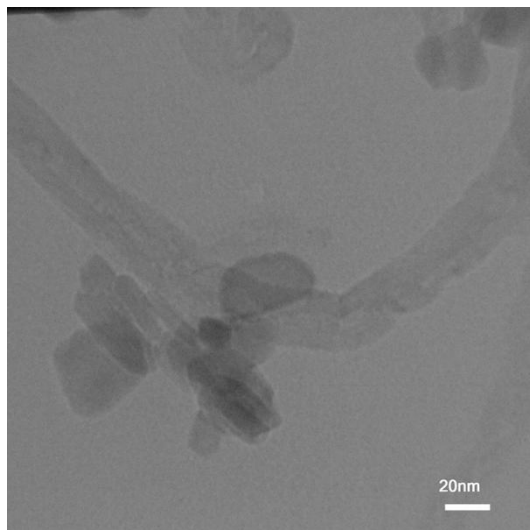


Figure 2. TEM image of NiO/CNTs nanocomposite

3.2. Adrenaline electrochemical investigation

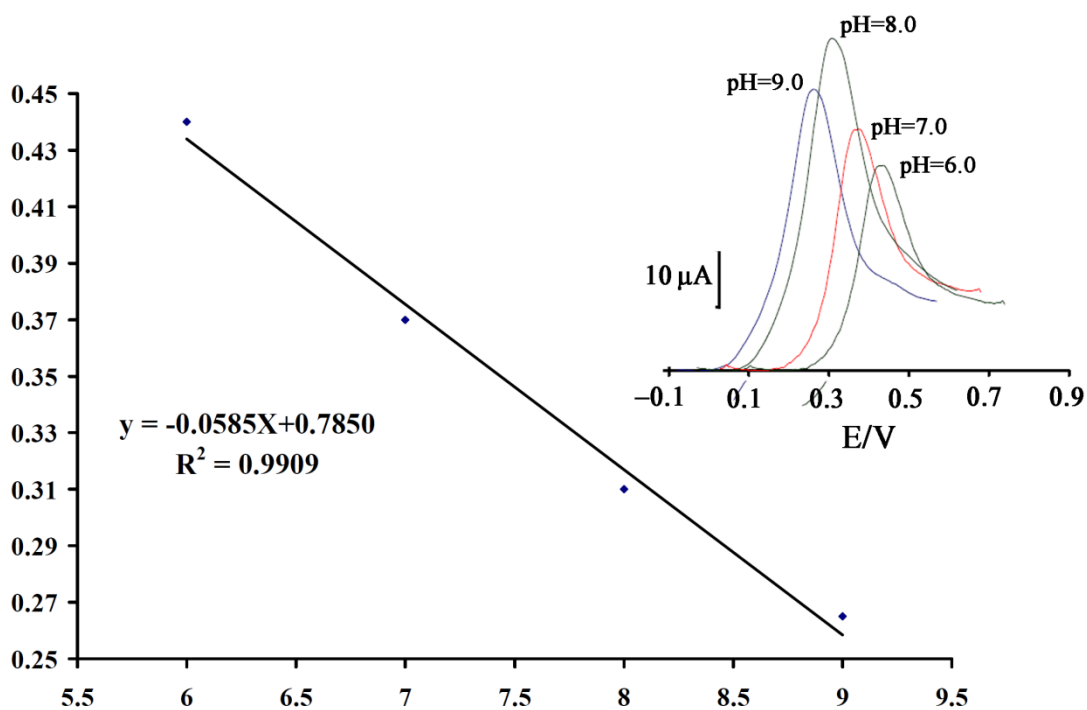


Figure 3. E–pH curve for electrooxidation of 100 μM adrenaline at CPE/NiO/CNTs. Insert: square wave voltammograms of 100 μM adrenaline at CPE/NiO/CNTs at different pH.

The active surface area of the CPE/NiO/CNTs and CPE were determined by Randles–Sevcik equation in the presence of 1.0 mmol L⁻¹ K₄Fe(CN)₆ in 0.10 mol L⁻¹ KCl. They were 0.284 and 0.33 cm² for CPE and CPE/NiO/CNTs, respectively.

Due to catechol structure of adrenaline, the electro-oxidation of adrenaline is depends on pH solution. Figure 3 showed the plot of E_p vs. pH value for electro-oxidation of adrenaline obtained from figure 3 insert voltammograms. As can be seen, a slope of -58.5 mV/pH was obtained for adrenaline that suggests two electron and two-proton for electrochemical reaction of adrenaline. Also, maximum oxidation signal was obtained at pH=8.0 that was used as optimum condition for other investigation.

Fig. 4 inset shows the current density derived from the square wave voltammograms of $100 \mu\text{M}$ adrenaline (pH 8.0) at the surface of different electrodes. The results show that the presence of NiO/CTs causes the good conductivity of the electrode. Figure 4 showed the electrochemical $100 \mu\text{M}$ adrenaline at a surface of CPE/NiO/CNTs (curve a) and CPE (curve b) at an optimum condition. At CPE/NiO/CNTs, and CPE, adrenaline showed oxidation signal, with E_{pa} of 0.3 V, and 0.34 V, respectively. On the other hand, the oxidation peak current of adrenaline at CPE/NiO/CNTs was higher than that compare to CPE. Thus, the CPE/NiO/CNTs exhibited a good catalytic activity toward the oxidation of adrenaline.

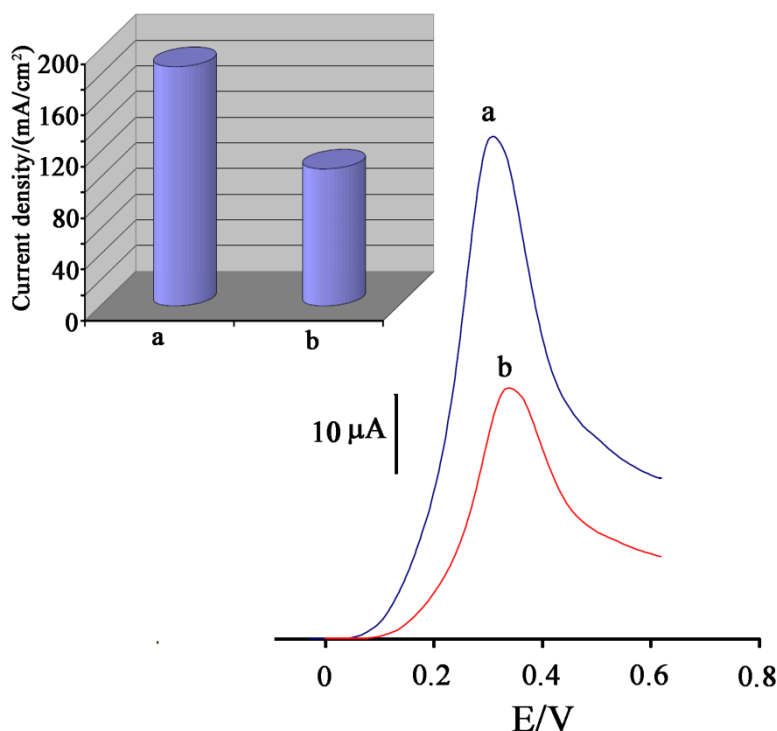


Figure 4. Square wave voltammograms of a) CPE/NiO/CNTs and b) CPE in the presence of $100 \mu\text{M}$ adrenaline at pH 8.0, respectively. Insert: the current density derived from square wave voltammograms.

Fig. 5 shows dependent of oxidation peak current with scan rate ($v^{1/2}$) in the presence of $600 \mu\text{M}$ adrenaline at the CPE/NiO/CNTs. There are good linear relationships between the peak currents and $v^{1/2}$ that confirm diffusion-controlled process for oxidation of adrenaline [51-55].

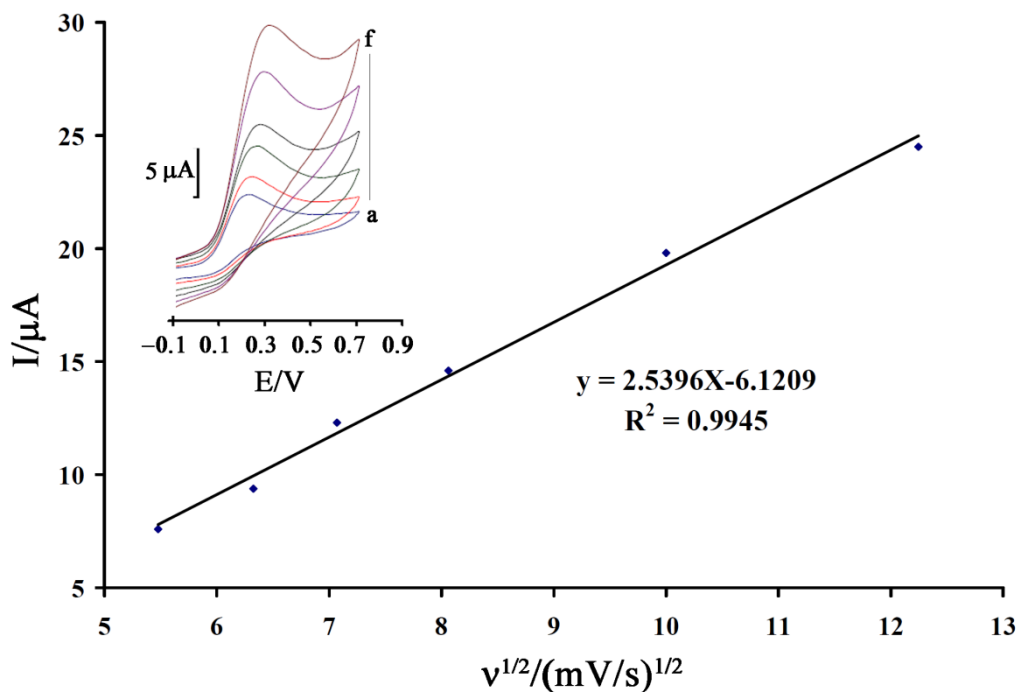


Figure 5. Plot of I_{pa} versus $v^{1/2}$ for the oxidation of adrenaline at CPE/NiO/CNTs. Inset shows cyclic voltammograms of adrenaline (600 μM) at CPE/NiO/CNTs at different scan rates of 30, 40, 50, 65, 100 and 150 mVs^{-1} in 0.1 M phosphate buffer, pH 8.0

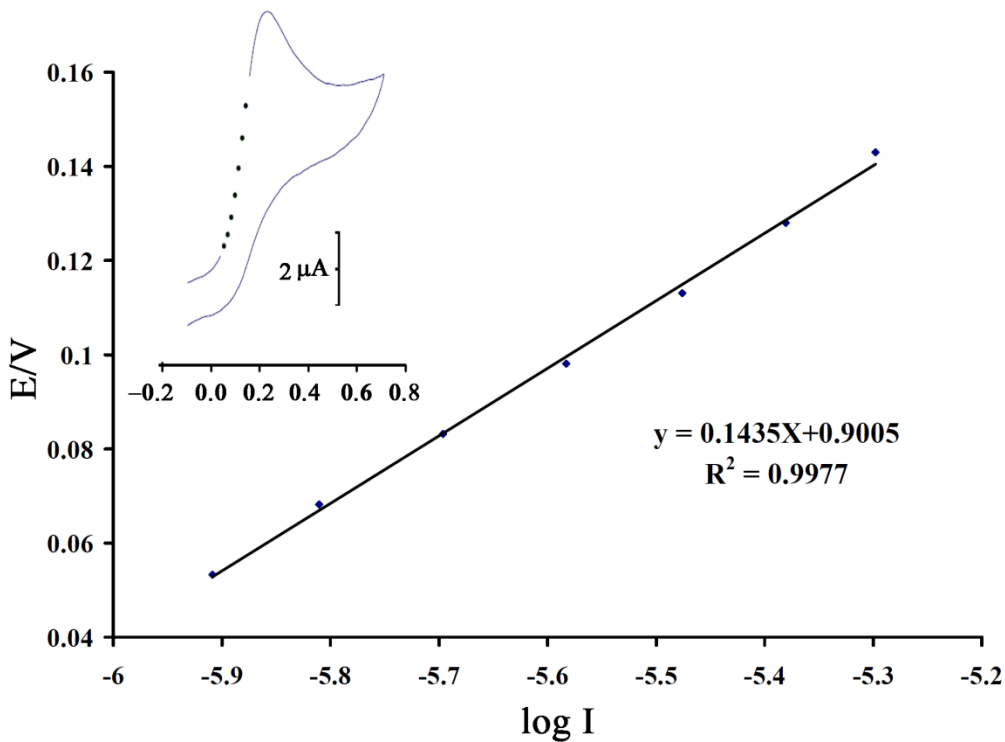


Figure 6. Tafel plot for CPE/NiO/CNTs in 0.1 M PBS (pH 8.0) with a scan rate of 30 mVs^{-1} in the presence of 600 μM adrenaline.

In continuous, a Tafel investigation was developed for analysis of kinetic parameter of adrenaline at a surface of CPE/NiO/CNTs (Fig. 6). The slope of the Tafel plot is equal to $n(1-\alpha)F/2.3RT$ which comes up to $0.1435 \text{ V decade}^{-1}$. We obtained α as 0.79.

Chronoamperometric measurements of adrenaline at CPE/NiO/CNTs were carried out by setting the working electrode potential at 400 mV in the presence of adrenaline at optimum condition (Fig. 7A). Experimental plots of I vs. $t^{-1/2}$ were employed for determination of diffusion coefficient D (Fig. 7B). From the resulting slope and Cottrell equation the mean value of the D was found to be $4.72 \times 10^{-6} \text{ cm}^2/\text{s}$.

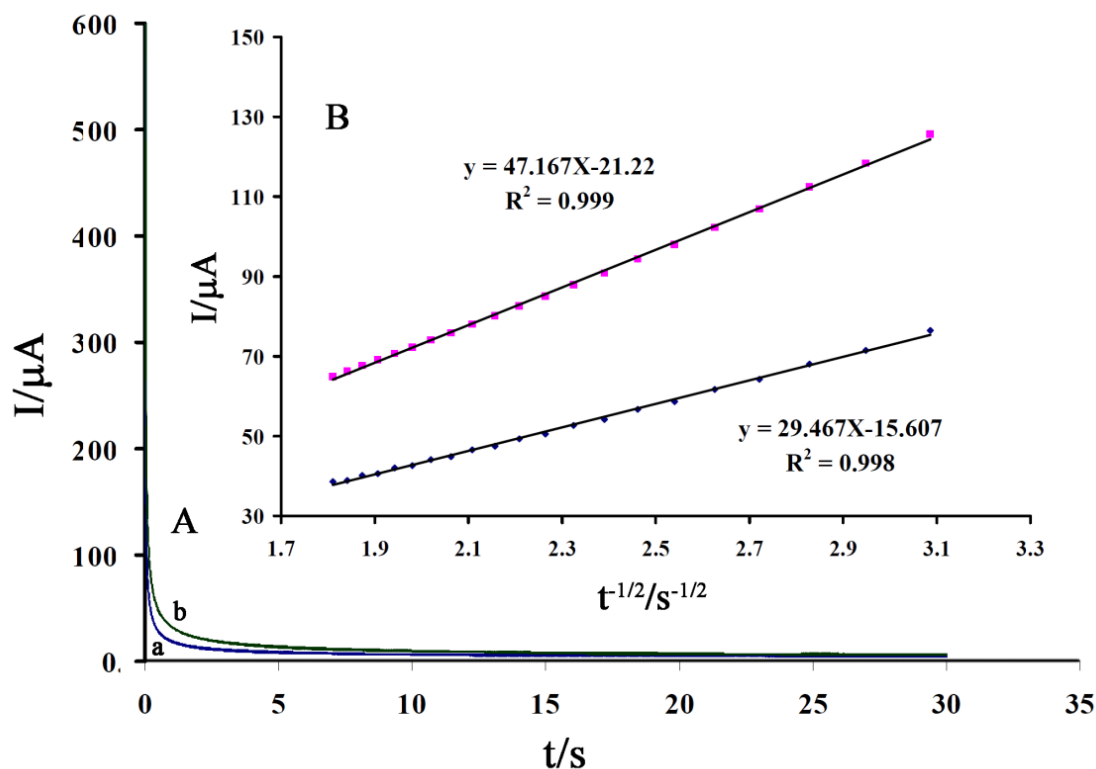


Figure 7. (A) Chronoamperograms obtained at CPE/NiO/CNTs in the presence of (a) 500 and (b) 600 μM adrenaline in the buffer solution (pH 8.0). (B) Cottrell's plot for the data from the chronoamperograms.

The square wave voltammograms show a linear relation between peak current and adrenaline concentration in the range 0.08–900 μM (Figure 8). The detection limit was 0.01 μM adrenaline according to the definition of $Y_{\text{LOD}} = Y_{\text{B}} + 3\sigma$.

The influence of biological and pharmaceutical interferences on adrenaline oxidation signal was studied in the presence of 20.0 μM adrenaline. The obtained data are presence in Table 1 that confirmed the CPE/NiO/CNTs has good selectivity for determination of adrenaline.

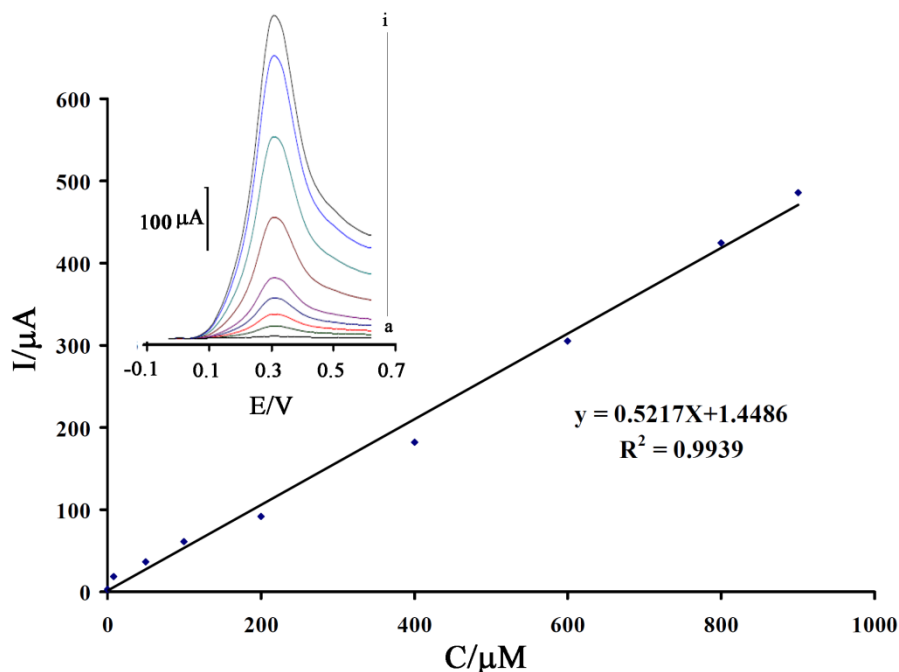


Figure 8. The plots of the oxidation peak current as a function of adrenaline concentration. Inset shows the SWVs of CPE/NiO/CNTs in 0.1 M PBS (pH 8.0) containing different concentrations of adrenaline. From inner to outer (a–i) correspond to 0.08, 8.0, 50.0, 100.0, 200.0, 400.0, 600.0, 800.0 and 900.0 μM of adrenaline.

Table 1. Interference study for the determination of 20 μM adrenaline.

Species	Tolerante limits ($W_{\text{Substance}}/W_{\text{Analytes}}$)
Glucose, Phenylalanine, Glutamic acid, Lucine	1000
Ascorbic acid*, NO_3^- , K^+ , Na^+ , Cl^-	800
Starch	Saturation

* Ascorbic acid interference can be minimize using ascorbic oxidase

Table 2. Determination of adrenaline in real samples (n=3).

Sample	Added (μM)	Expected (μM)	Founded (μM)	Published method (μM) [6]	F_{exp}	F_{tab}	t_{exp}	$t_{\text{tab}(95\%)}$
Ampule	—	5.0	4.73±0.43	5.43±0.57	7.5	19.0	1.7	3.8
	10.0	15.0	15.55±0.73	14.65±0.87	9.5	19.0	2.4	3.8
Urine	—	—	<LOD	<LOD				
	20.0	20.0	20.89±0.98	20.87±1.01	13.5	19.0	3.4	3.8

±Shows the standard deviation.

Finally the ability of CPE/NiO/CNTs was checked for the voltammetric determination of adrenaline in real samples. The obtained data was also compared with a other work [6], the results of which are given in Table 2.

4. CONCLUSION

NiO/CNTs nanocomposite was synthesized and incorporated onto the surface of a carbon paste electrode as a highly sensitive sensor for adrenaline analysis. The NiO/CNTs was characterized with TEM and XRD methods. Compared with adrenaline signal at CPE, high electrochemical activity was occur at a surface of CPE/NiO/CNTs, revealing some advantages of CPE/NiO/CNTs over CPE such as low charge transfer resistant. Finally, the CPE/NiO/CNTs were used for analysis of adrenaline in real samples.

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