

Full Paper

Simultaneous Determination of Dopamine and Acetaminophen by a Carbon Paste Electrode Doubly Modified with Poly (Pyrrole) and CuO Nanoparticles

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Received: 24 April 2016 / Received in revised form: 17 September 2016 /

Accepted: 19 September 2016 / Published online: 30 September 2016

Abstract- An electrochemical sensor was prepared by the modification of the carbon paste electrode (CPE) with a synthesized nanocomposite. The structure and morphology of the nanocomposite which was prepared by combination of poly pyrrole and copper oxide nanoparticles (PPy/CuO) was studied. This nanocomposite showed good electrocatalytic activity; so that the nanocomposite based electrochemical sensor (CPE-PPy/CuO) exhibited an excellent electroanalysis signals toward oxidation of dopamine (DA) and acetaminophen (AC). This effect is concluded from the high conductivity, low electron transfer resistance and catalytic effect of the PPy/CuO. The fabricated sensor had a lower overvoltage and higher electrical current respect to the bare CPE, for both DA and AC. Also, this sensor can resolve the overlapped anodic peaks of DA and AC and therefore it was used in the simultaneous determination. The calibration plots with wide linear ranges and suitable sensitivity was obtained for DA and AC by differential pulse voltammetry. Also good detection limits were found including 0.020 μM for DA and 0.025 μM for AC. Finally, the electrochemical sensor was used for determination in real samples.

Keywords- Electrochemical sensor, Nanocomposite, Conducting polymer, Dopamine, Acetaminophen

1. INTRODUCTION

Dopamine (DA) is an important neurotransmitter which made by nerve tissue (including the brain) and the adrenal gland [1]. Also DA can be supplied as a medication that acts on the sympathetic nervous system, producing effects such as increased heart rate and blood pressure. However, high catecholamine levels can leading to rapid heart rate, high blood pressure, and possible death of the heart muscles [2]. In contrast, a deficiency of DA in the basal ganglia, is related to Parkinson's disease and also Schizophrenia [3,4]. Therefore, determination of dopamine in physiological samples with high sensitivity and selectivity is of great clinical significance. Different analytical methods have been reported for DA [5,6].

Acetaminophen (AC) is a most extensively employed drug as pain reliever and fever reducer. AC is used for minor aches and pains, and is a major ingredient in numerous cold and flu medicines and also it can be used in the management of cancer or postoperative pain [7]. It is generally safe for human use at recommended doses. But overdoses, chronic use or concomitant use of AC with alcohol or other drugs can cause serious side effects such as liver damage and may lead to death [8,9]. Various methods are presented for determination of AC in pharmaceutical formulations and in biological fluids [10-12].

The in vitro studies have indicated that the use of AC protects dopaminergic neurons from the oxidative stress damage caused by acute exposure to higher levels of DA [13]. Also, the prolonged dosage of AC has been found to significantly reduce the levels of DA [14]. Thus, the simultaneous analysis of DA and AC in biological fluids is of interest to understand their clinical and pharmacological importance.

Many instrumental methods have been applied for determination of biological and medicinal substances. Most of these instrumental techniques are sample-consuming or require sample pretreatment or have lengthy analysis times and high costs [3]. While, electrochemical methods offer a powerful tool for determination of biochemical substances such as DA [15] or medicinal substances like AC [16] without those disadvantages [17-19]. Also, the uses of modified electrodes in electrochemical methods bring numerous advantages including selective pre-concentration, selective recognition and electrocatalysis [20,21].

Electrocatalysis at nanocomposite based modified electrodes offer significant advantages for the determination of many drugs and bio-substances. These electrodes can enhance the electron transfer rate and reduce the overpotential of the oxidation of many substances [22,23]. Therefore these modified electrodes can be used as electrochemical sensors in clinical, medical, industrial, environmental and agricultural analyses [21,24].

Nanostructured materials have aroused dramatic interests and have become an intensive research area for the past decade due to their unique properties [25,26]. Among these materials, nanostructured conducting polymers received an ever increasing attention [22]. Conducting polymers can be used as a matrix for accommodating metal oxide nanoparticles. The resulted nanostructure can be used in bulk or surface modification of the electrodes

[22, 27,28]. Among the metal oxide nanoparticles, copper oxide (CuO) widely used in numerous applications such electrochemical sensors [29,30] because of its high specific surface area and good electrochemical activity [31,32].

In this paper, because of catalytic activity of CuO and unique properties of poly pyrrole (PPy), a PPy/CuO nanocomposite was synthesized. After verification of PPy/CuO nanocomposite, an electrochemical sensor was fabricated by it (CPE-PPy/CuO). The electrocatalytic determination of DA and AC was studied at this modified electrode. The novelty of this work is preparing an electrochemical sensor by the modification of the carbon paste electrode with the synthesized nanostructured poly pyrrole doped with copper oxide nanoparticles. So that, very interesting linear ranges and detection limits for DA and AC together with their simultaneous determination was obtained by this sensor. The inexpensive electrode with simple preparation method together with the high sensitivity and selectivity make the modified electrode as an excellence electrochemical sensor.

2. EXPERIMENTAL

2.1. Apparatus and reagents

Electrochemical measurements were performed by a potentiostat/galvanostat (SAMA 500, electroanalyzer system, I.R. Iran). All electrochemical measurements were carried out in a three electrode cell including modified or bare CPE, saturated calomel electrode (SCE) and a platinum wire as working, reference and counter electrodes, respectively. The pH value of solutions was adjusted using a Milwaukee pH meter. The morphology of the nanocomposites was analyzed by scanning electron micrographs (SEM) using a Philips XL30 scanning electron microscopy (Holland). FT-IR spectra of the samples were recorded at 4 cm^{-1} resolution with a Nicolet 100 Fourier transform infrared (FT-IR) spectrometer.

All solutions were freshly prepared with deionized water. Phosphate buffers were prepared from orthophosphoric acid and its salts (Merck, Germany). The graphite fine powder and paraffin oil (DC 350, 0.88 g cm^{-3}), both from Merck (Germany), were used as received. Pyrrole (Fluka, Switzerland) was distilled and stored in a refrigerator in dark prior to use. DA and AC and all other reagents were from Sigma-Aldrich.

2.2. PPy/CuO nanocomposite synthesize

The 20 ml solution of copper chloride (0.1 M) and pyrrole (0.1 M) was prepared with double distilled water. The solution was stirred in a magnetic stirrer at room temperature for 1h. FeCl_3 solution 0.2 M (10 ml) was dissolved in the above solution under stirring the mixture. After stirring, pH value of the solution was increased to 10 by adding aqueous ammonia (NH_3). The solution was started to boil at about 90°C . After 50 min boiling, the

synthesized nanocomposites were centrifuged, separated and rinsed in double distilled water for about 5 min in an ultrasonic bath.

2.3. Fabrication of the CPE-PPy/CuO electrochemical sensor

The PPy/CuO modified carbon paste electrodes were prepared by mixing 0.05 g of PPy/CuO, 0.95 g of graphite powder and appropriate amount of paraffin oil with a mortar and pestle until a uniform paste was obtained. The paste was then packed into the end of a plastic tube (3.5 mm i.d. and 10 cm long). The electrical contact was provided by inserting a copper wire into the carbon paste. This electrode was used as electrochemical sensor. The unmodified carbon paste electrode was prepared in the same way without adding PPy/CuO.

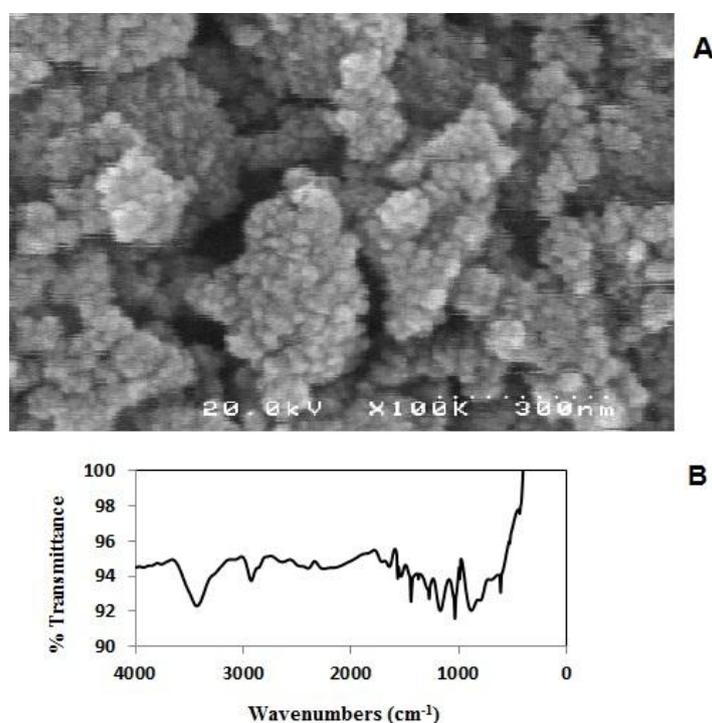


Fig. 1. A) SEM image of the PPy/CuO composite; B) FT-IR spectrum of PPy/CuO composite. Also the electrochemical characterization of the PPy/CuO was performed by recording the cyclic voltammograms of CPE-PPy/CuO and bare CPE in buffer solution pH 7.0. These voltammograms are shown at Fig. 2 curve (a) and curve (b), respectively. As can be seen the background current of CPE-PPy/CuO is increased in comparison with bare CPE, which can be related to the high surface area of the nanocomposite PPy/CuO [37]

3. RESULTS AND DISCUSSION

3.1. Characterization of PPy/CuO nanocomposite

The morphology and particle size information of the PPy/CuO nanocomposite could be obtained with the electron microscopy characterization methods. The resulting morphology

of the synthesized PPy/CuO nanocomposite powder from SEM could be seen from Fig. 1A. This figure shows that PPy/CuO nanocomposite is seeds shape in the range of 30-120 nm.

Fig. 1B shows IR spectrum of PPy/CuO composite. The peaks at 1565 cm^{-1} and 1442 cm^{-1} corresponding to the fundamental vibrations of polypyrrole ring. The bands at 1272 , 1033 cm^{-1} may correspond to =C–H band in plane vibration. The broad band at 1373 cm^{-1} may be assigned for N–C stretching band. Peak at 1373 cm^{-1} may be considered due to –N–C stretching mode of vibrations [33-35]. Absorption peaks at 1635 and 1373 cm^{-1} for typical pyrrole ring vibration. The peaks at 609 , 524 , 987 and 433 cm^{-1} show presence of polymerized pyrrole and CuO band [36]. Also the electrochemical characterization of the PPy/CuO was performed by recording the cyclic voltammograms of CPE-PPy/CuO and bare CPE in buffer solution pH 7.0. These voltammograms are shown at Fig. 2 curve (a) and curve (b), respectively. As can be seen the background current of CPE-PPy/CuO is increased in comparison with bare CPE, which can be related to the high surface area of the nanocomposite PPy/CuO [37].

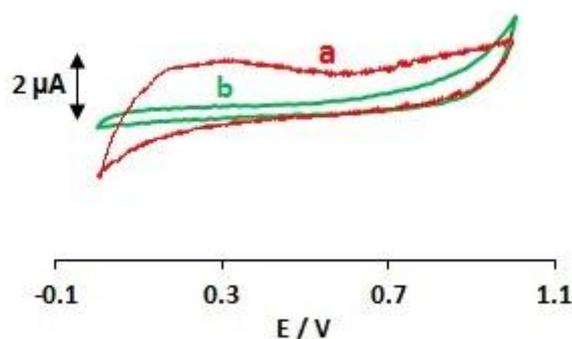


Fig. 2. Cyclic voltammograms of the CPE-PPy/CuO (curve a) and bare CPE (curve b) at scan rate of 50 mVs^{-1} and in phosphate buffer solution pH 7.0

3.2. The catalytic effect of CPE-PPy/CuO on the oxidation of DA and AC

The electrochemical oxidation of DA at modified and unmodified electrodes was investigated by cyclic voltammetry. The curves (a) and (b) in Fig. 3A show the cyclic voltammetric responses of 1.0 mM DA at CPE-PPy/CuO (curve a) and bare CPE (curve b) at scan rate of 50 mVs^{-1} in phosphate buffer solution pH 7.0. The anodic peak potential of DA oxidation is about 400 mV at bare CPE (Fig. 3A curve b), while it is decreased to the potential of about 200 mV at CPE-PPy/CuO (Fig. 3A curve a). Also, the anodic peak current of DA is significantly improved at the CPE-PPy/CuO. Therefore, the PPy/CuO nanocomposite shows efficient catalytic effect to the oxidation of DA. Moreover, the PPy/CuO provides large surface area at the modified electrode.

The catalytic effect of PPy/CuO was investigated for AC electro-oxidation, too. Curve (a) in Fig. 3B shows that the anodic peak potential of AC is about 420 mV at CPE- PPy/CuO, whereas the oxidized potential of AC is about 520 mV at bare CPE (curve b). Also, the anodic peak current of AC is enhanced at the CPE-PPy/CuO. Therefore, the oxidation reaction of AC can be catalyzed at CPE-PPy/CuO.

The results show that the presence of PPy/CuO nanocomposite at the electrode led to great improvement in the electrochemical responses of DA and AC. The nanocomposite modified electrode can decrease the overpotential and enhance the peak current for both substances. The PPy conducting polymer is beneficial to electrons transfer and the CuO nanoparticles promote electrons to the substances at the electrode surface. Therefore, CPE-PPy/CuO offers a favorite electrode for oxidation of DA and AC because of low resistance, catalytic effect of CuO, nanometer size and large accessible surface area.

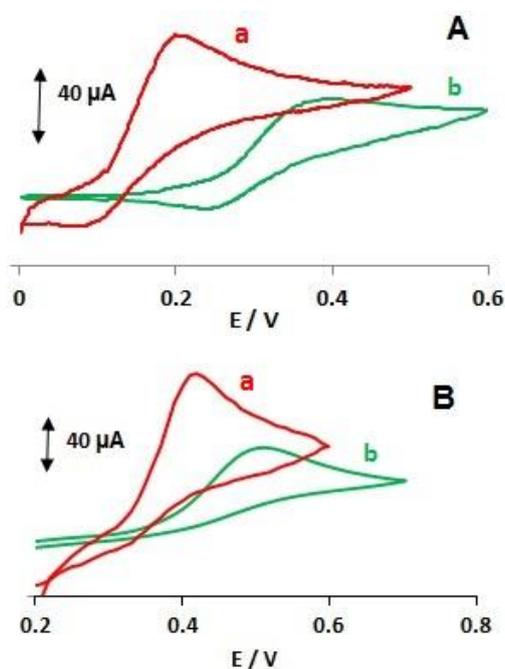


Fig. 3. Cyclic voltammograms of A) 1.0 mM DA and B) 1.0 mM AC at CPE-PPy/CuO (curves a) and bare CPE (curves b); in all cases scan rate is 50 mVs^{-1} and solution is phosphate buffer with pH 7.0

3.3. The effect of the potential scan rate on the oxidation of DA and AC

The effect of the potential scan rate was investigated on the oxidation of DA and AC at the surface of CPE-PPy/CuO. The Fig. 4A displays the cyclic voltammograms of DA at different scan rates on the surface of CPE-PPy/CuO. The anodic peak current (I) versus the square root of scan rate ($v^{1/2}$) is plotted in the Fig. 4B. The linear behavior at this plot in the

range of 25–150 mVs^{-1} indicates the electrochemical oxidation of DA at CPE-PPy/CuO is diffusion controlled [38].

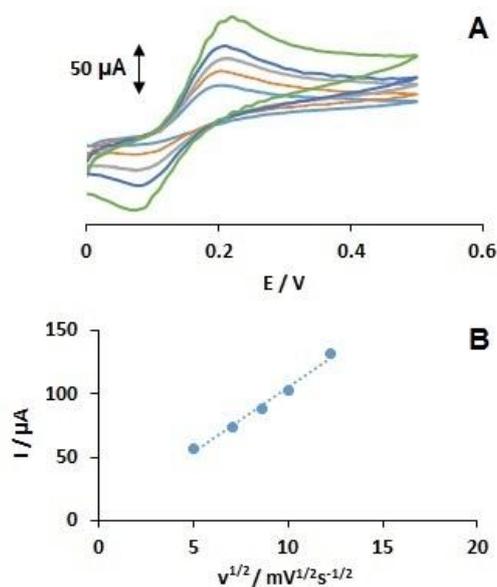


Fig. 4. A) Cyclic voltammograms of 1.0 mM DA at different scan rate in the range of 25-150 mVs^{-1} ; B) The plot of anodic peak current versus the square root of scan rate

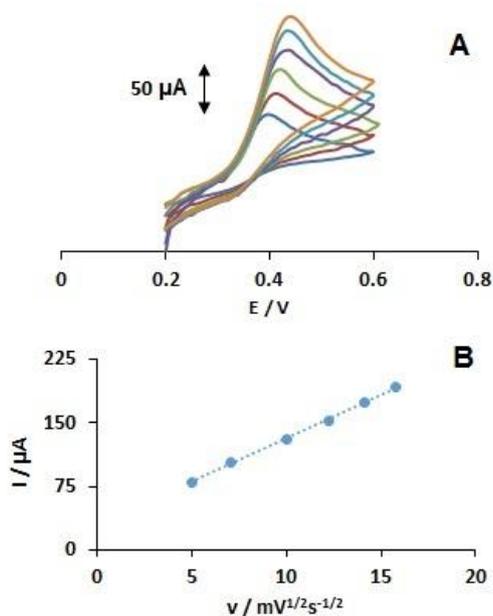


Fig. 5. A) Cyclic voltammograms of 1.0 mM AC at different scan rate in the range of 25-250 mVs^{-1} ; B) The plot of anodic peak current versus the square root of scan rate

The Fig. 5 shows the cyclic voltammograms and also the plot of $I-v^{1/2}$ for AC. As can be seen the peak current of the cyclic voltammograms is increased with increasing the potential scan rate (Fig. 5A). The relationship between peak current and square root of potential scan rate is linear as indicated in Fig. 5B. Therefore the electrochemical oxidation of AC at CPE-PPy/CuO is diffusion controlled similar to the DA.

3.4. Calibration plots of DA and AC

Since the CPE-PPy/CuO can catalyze the oxidation reaction of DA and AC therefore this electrode can be used as an electrochemical sensor for determination of both substances. The technique of differential pulse voltammetry (DPV) was used to obtain the calibration plots of the CPE-PPy/CuO for DA and AC. For this purpose, the DP voltammograms of different concentrations of each substance were recorded. Then the peaks currents were plotted versus the concentrations and the calibration plot was constructed. The calibration plot for DA had two linear segment including 0.060–20.0 μM and 20.0–1000.0 μM . The slopes of these linear equations are 0.689 $\mu\text{A}\mu\text{M}^{-1}$ for first segment and 0.055 $\mu\text{A}\mu\text{M}^{-1}$ for second segment. For AC, the calibration plot was in the ranges of 0.030–40.0 μM and 40.0–1250.0 μM , with the corresponding slopes of 0.522 $\mu\text{A}\mu\text{M}^{-1}$ and 0.052 $\mu\text{A}\mu\text{M}^{-1}$, respectively. The detection limits were calculated as 0.020 μM for DA and 0.025 μM for AC.

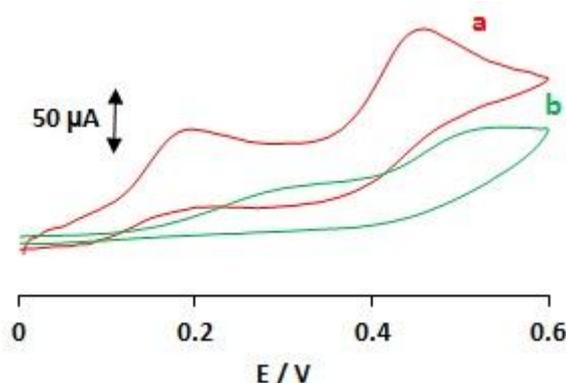


Fig. 6. Cyclic voltammograms of a solution containing DA and AC at CPE-PPy/CuO (curve a) and bare CPE (curve b); scan rate is 50 mVs^{-1} and solution is phosphate buffer with pH 7.0

3.5. Simultaneous determination of DA and AC

The capability of the PPy/CuO based electrochemical sensor was studied for simultaneous determination of DA and AC. At first, the cyclic voltammograms of a solution containing both substances was recorded at CPE-PPy/CuO and also bare CPE (Fig. 6). As can be seen, at the bare CPE an overlapped cyclic voltammogram was obtained (curve b), while at the CPE-PPy/CuO the electrochemical responses of DA and AC were separated (curve a).

Also the peak current of the oxidation of these substances significantly increased at the CPE-PPy/CuO.

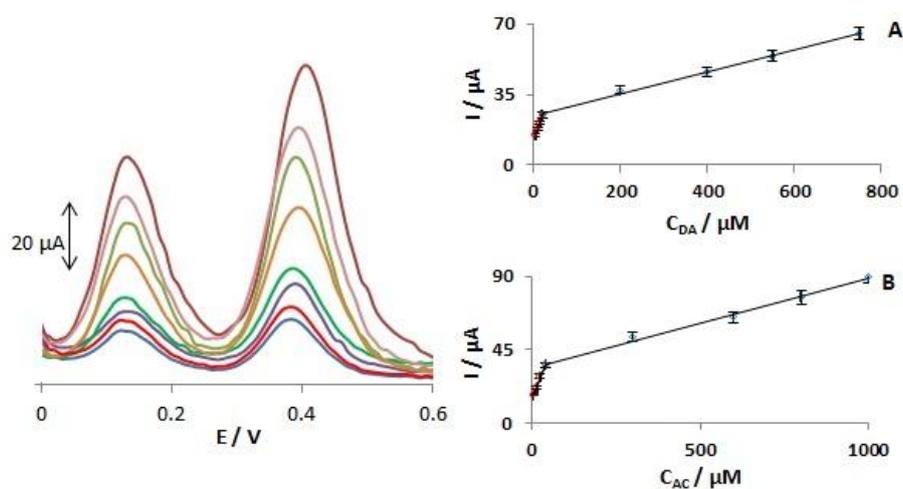


Fig. 7. Differential pulse voltammograms of CPE-PPy/CuO in phosphate buffer solution (pH 7.0) containing different concentrations of DA+AC, from inner to outer: 5.0+5.0, 10.0+15.0, 15.0+25.0, 20.0+40.0, 200.0+300.0, 400.0+600.0, 550.0+800.0, 750.0+1000.0 in μM respectively; Insets: calibration plots of A) DA and B) AC

The simultaneous determination of DA and AC at CPE-PPy/CuO was performed by recording the DP voltammograms in solution with different concentrations of the substances (Fig. 7).

Table 1 Comparison of the performance of the CPE-PPy/CuO for determination of DA and AC with some other electrochemical sensors

Electrode Modifier		LR ^a for DA (μM)	DL ^b for DA (μM)	LR for AC (μM)	DL for AC (μM)	Ref.
GCE ^c	Porous gold nanosheets	2.0 - 298.0	0.28	3.0 - 320.0	0.23	[39]
CPE	HMWCNT ^d	0.2-1000.0	0.06	NA ^e	NA	[40]
GCE	CoNPs/MWCNT ^f	0.0050–3.0	0.015	0.0052–0.45	0.001	[41]
CCE ^g	graphene nanoplatelets and ionic liquid	0.1–20	0.068	0.1–20	0.063	[42]
GCE	NiO–CuO/GR ^h	0.5–20	0.17	4–400	1.33	[43]
CPE	PPy/CuO	0.060–1000.0	0.020	0.030-1250.0	0.025	This work

^a LR: linear range; ^b DL: detection limit; ^c GCE: glassy carbon electrode; ^d HMWCNT: Hematoxylin multi-walled carbon nanotubes; ^e NA: Not available; ^f CoNPs/MWCNT: Multi-walled carbon nanotubes functionalized by cobalt nanoparticles; ^g CCE: carbon-ceramic electrode; ^h NiO–CuO/GR: nickel oxide and copper oxide nanoparticles–graphene composite film

The Fig. 7 shows two completely separated peaks were obtained at potentials of 120 and 400 mV, corresponding to the oxidation of DA and AC. The peak currents are increased with increasing the concentration. The obtained calibration plots of these substances in simultaneous determination are shown in the insets of Fig. 7. The slopes of the linear equations are $0.690 \mu\text{A}\mu\text{M}^{-1}$ and $0.054 \mu\text{A}\mu\text{M}^{-1}$ for DA and are $0.517 \mu\text{A}\mu\text{M}^{-1}$ and $0.053 \mu\text{A}\mu\text{M}^{-1}$ for AC. As can be seen, the slopes of the calibration plots for DA and AC in simultaneous determination are similar to the obtained slopes in single determination. Therefore, the CPE-PPy/CuO can be used for simultaneous determination of DA and AC without interference.

The kind of the electrode, the modifier, linear range and detection limit of some electrochemical sensors are compared with the present work at Table 1. As can be seen, the proposed electrode in this work has better detection limit and linear range for both DA and AC excluding reference [41].

3.6. Application in real sample

As discussed at the introduction section, the simultaneous determination of DA and AC in real samples is very important. Therefore, for investigating the applicability of the CPE-PPy/CuO in electroanalysis of real samples, this sensor was applied for simultaneous determination of DA and AC in solutions with different matrix. The distilled water was used as the first matrix to test the accuracy of the determination by the sensor. Then, the determination was done in the aqueous solution of some blood serum components including Na^+ , K^+ , SO_4^{2-} , NO_3^- , Cl^- , CO_3^{2-} , glucose and some amino acids including alanine, arginine, asparagine, serine, threonine, valine, leucine, glycine, and tyrosine with concentration of $100 \mu\text{M}$. This matrix was used for checking the performance of the sensor in simultaneous determination in the biological fluids.

Table 2. Application of CPE-PPy/CuO for determination of DA and AC in real samples

Matrix	Sample number	Added (μM)		Recovery (%)		RSD (%)	
		DA	AC	DA	AC	DA	AC
Water	1	0.0	0.0	-	-	-	-
	2	15.0	25.0	103	98	2.5	3.1
	3	60.0	60.0	97.7	103.2	3.0	1.7
solution of blood serum components	1	0.0	0.0	-	-	-	-
	2	60.0	60.0	102.5	103.1	3.5	3.3
	3	150.0	150.0	99.8	98.5	3.0	2.9

Determination of real samples was performed by DPV technique and standard addition method. The recovery percent and relative standard deviation (RSD) were calculated. The results for determination of DA and AC in real samples are given in Table 2 with satisfactory recovery percent and good RSD.

4. CONCLUSIONS

A nanocomposite of conducting polymer, poly pyrrole, and copper oxide nanoparticles was prepared and an electrochemical sensor was fabricated based on it. The nanocomposite based sensor showed good electrocatalytic activity toward oxidation of DA and AC. The anodic peak currents of these substances were enhanced and the oxidation potentials of them were decreased at the sensor. The electrochemical sensor was used for electroanalytical determination of DA and AC and low detection limits and wide linear ranges were obtained for them. Also this electrochemical sensor showed high selectivity and good resolution in simultaneous determination of DA and AC. The proposed sensor was used successfully for determination in real samples.

Acknowledgements

The authors would like to thank National Elites Foundation of Iran for financial support of this research and also wish to thankful Urmia University and Shahid bakeri high education center.

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