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Full Paper

SnO_2/α-Fe_2O_3 Hierarchical Nanorods Modified Carbon Paste Electrode as the Novel Sensor for Sensitive Simultaneous Determination of Dopamine and Tramadol

Ameneh Vazirirad,[1] Ali Babaei,[1,2,*] and Mohammad Afrasiabi[1]

[1]Department of Chemistry, Faculty of Science, Arak University, Arak, I.R. Iran
[2]Institute of Nanosciences & Nanotechnology, Arak University, Arak, I.R. Iran

*Corresponding Author, Tel.: +98 863 2627532
E-Mails: ali-babaei@araku.ac.ir & ali.babaei08@gmail.com

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Abstract- A chemically modified carbon paste electrode (CPE) based on SnO_2/α-Fe_2O_3 hierarchical nanorods (SFOHNRs) were constructed as a novel simple electrochemical sensor for a sensitive simultaneous determination of dopamine (DA) and tramadol (TRA). To investigate electrochemical behaviours of DA and TRA several techniques such as differential pulse voltammetry (DPV), cyclic voltammetry (CV) and chronoamperometry (CA) methods were used. SFOHNRs were fabricated via three step process. In order to characterize SFOHNRs several techniques such as field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) technique and energy dispersive X-ray spectroscopy (EDX) were used. Application of SFOHNRs as the modifier of the CPE (SFOHNRs/CPE) showed high oxidation peak currents for determination of DA and TRA due to its catalytic effect and its high surface area. Using DPV technique, the sensor showed linear ranges of 0.1-70 µM and 0.5-65 µM and low detection limits of 40 nM and 65 nM toward DA and TRA, respectively. The fabricated sensor exposed excellent sensitivity, simplicity and high selectivity toward simultaneous determination of DA and TRA. The analytical performance of the sensor has been evaluated for analysis of DA and TRA in human blood serum and urine with satisfactory results.

Keywords- SnO_2/α-Fe_2O_3 Hierarchical Nanorods; Modified carbon paste electrode; Electrochemical sensor; Dopamine; Tramadol

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1. INTRODUCTION

Nowadays there are several studies in application of nanostructural materials due to their unique properties. Among these materials there are more attention on application of one dimential nanostuctral materials like nanofibers, nanowires and nanorods because of their potential in use as nanotools [1].

High demands in application of nanomaterials lead to more attentions in development of strategies to synthesize nanostructures with tunable and various properties. According to this requirements, application of several materials with new properties such as core–shell, hetero- and/or doped structures were considered [2]. Among these materials SnO_2 and Fe_2O_3 nanostructures were increased more attentions in applications in photocatalytic degradation [3], gas sensing [4,5], and lithium-ion batteries (LIBs) [6,7]. The latest investigations revealed that physical properties of SnO_2 or Fe_2O_3 can be extremely developed by forming Fe_2O_3–SnO_2 heterostructures [8,9]. Until now three types of core–shell [10,11], branched [12,13], and random [14,15], Fe_2O_3–SnO_2 heterostructures are known. Among these three types of heterostructures, branched nanostructures own two excellent deserves. The first one is a well-defined border and the second one is high surface area. Therefore, for the first time we decide to use synthesized branched Fe_2O_3–SnO_2 nanostructure as a novel modifier in carbon paste electrode (CPE).

There is significant attention in developing researches on neurotransmitters such as dopamine (DA). DA is a important neurotransmitter (NTM) in mammalian brain tissues that acts an significant physiological role in the functioning of central nervous sytems [16,17]. DA is also involved in neurological illness like Parkinson’s, Alzheimer’s disease [18] and Schizophrenia [19] In addition it has been suggested that DA plays a role in drug addiction and some sign of HIV [20].

Tramadol (TRA) is a centrally used as strong pain reliever which has become the most advised opioid in worldwide [21]. However, this medicine has some time disadvantages such as risk for breathing disorder [22] and drug addiction [23]. Therefore, this drug must be used with right dosage as prescribed [24,25]. However, there are some reports on TRA abuse and TRA related fatalities [26]. Its total analgesic usefulness is similar to that attained using equianalgesic doses of morphine or alfentanil [27]. There is a report that use of TRA could alters brain dopamine that perhaps related to its antidepressant potency [28].

A range of techniques such as chromatographic methods [29], mass spectroscopy [30], fluorescence [31], spectrophotometry [32], chemiluminesence [33] and electrochemical methods [34] are reported in the literature for detection of DA. For the determination of TRA, a few analytical methods such as chromatography [35], spectrophotometry [36], spectrofluorometry [37] and electrochemical techniques [38] were reported. However, some of these non-electrochemical methods suffer from some disadvantages including long analysis times, high costs, the requirement for sample pretreatment, and in some cases low sensitivity and selectivity. These disadvantages make them unsuitable for routine analysis. As far as our knowledge, there is no report on electrochemical simultaneous determination of DA and TRA. For these reasons, development of a simple, inexpensive, sensitive and accurate analytical method for simultaneous determination of DA and TRA would be of considerable value.

By considering high surface area and catalytic properties of $SnO_2/\alpha\text{-}Fe_2O_3$ hierarchical nanorods (SFOHNRs), in this work we repot for the first time application of SFOHNRs as modifier of carbon paste electrode (CPE) to fabricate SFOHNRs/CPE as a novel electrochemical sensor for simultaneous determination of DA and TRA. The application of the sensor was examined by analyzing human blood serum and urine as the real samples which showed satisfactory results.

2. EXPERIMENTAL

2.1 Chemicals and Apparatus

DA and TRA were obtained from Sigma-Aldrich chemical company, respectively. Other chemical compounds were purchased from Merck chemical company. All chemicals were analytical grade and used without further purification. Triply distilled water was used to prepare all aqueous solutions. Ammonia buffer solution (ABS) as the supporting electrolyte was prepared by mixing appropriate amounts of 0.1 M NH_3, 0.1 M NH_4Cl solutions to obtain desired pH values.

All of electrochemical experiments were carried out using an AUTOLAB 30V device Potentiostat / Galvanvastat (ECO CHEMIE) using SFOHNRs /CPE as the working electrode, an Ag/AgCl/3M KCl electrode as the reference electrode and a platinum wire as an auxiliary electrode. Electrochemical data were recorded and analyzed using GPES software version 4.9. All solutions of included DA and TRA carried out 20 seconds of stirring prior to any voltammetric experiments. Metrohm 744 pH meter using a combination glass electrode was used to adjust pH of ABS. Fresh human urine and blood serum samples were supplied by a local pathology clinic. About 10 mL of the blood serum and urine samples were centrifuged; then, after filtering, they were diluted 10-times with ABS of pH 8 and applied to determine spiked DA and TRA in real sample without any further pretreatment. FE-SEM images were obtained on FEI Nova NanoSEM 450 microscope. The X-ray diffraction pattern was recorded by a Rigaku SmartLab instrument.

2.2 Synthesis of SFOHNRs

SFOHNRs were synthesized via a three-step process as previously reported [39]. Briefly, 40 ml solution of 0.5 M $FeCl_3$ was placed in an autoclave. The autoclave was heated to 120 ◦C for 12 h. The precipitates were washed several times with water and ethanol respectively. Finally, the precipitate was dried at 80 ◦C for 6 h to obtain $\beta\text{-}FeOOH$ nanorods. For calcinations, the precipitate was heated at 500 ◦C for 2.5 h to obtain α-Fe_2O_3 nanorods with porous structures. Finally, the SFOHNRs were synthesized using α-Fe_2O_3 nanorods and $SnCl_4$ as precursor materials using a hydrothermal method. For this purpose, 0.015 g of α-Fe_2O_3 nanorods were dispersed into a combined solution of heptane (10.2 ml), hexanol (3.0 ml), sodium dodecyl sulfate (SDS, 1.44 g), $Sn(OH)_6^{2-}$ (2.0 ml; the volume ratio of 0.5 M $SnCl_4$ and 5 M NaOH solutions is 1:3). Then the solution was sonicated for 5min and then it transferred to a Teflon-lined autoclave and then it heated at 220 ◦C for 6 h. Finally, the precipitate was washed several times with distilled water and ethanol to obtain SFOHNRs.

2.3 Preparation and optimization of modified SFOHNRs/CPE

The carbon paste modified with SFOHNRs was prepared by mixing the different amounts of graphite powder and SFOHNRs with appropriate amount of paraffin oil. Then the paste was packed into the end of an insulin syringe (i.d. 2 mm) and a copper rod was embedded into the paste to provide electrical connection. The prepared modified electrode was named as SFOHNRs/CPE. The unmodified carbon paste electrode was fabricated in a same way without addition of SFOHNRs and it was nominated as CPE.

In order to obtain high sensitivity in determination of DA and TRA, the amount of SFOHNRs as the modifier in the modified electrode was optimized (Fig. 1). As can be seen in Fig. 1a and 1b, by increasing SFOHNRs% the oxidation peaks for 30 µM TRA and 15 µM DA were increased from 2.5% up to 10% and then they decreased by increasing of SFOHNRs up to 30%, respectively. Therefore, composition of 10% SFOHNRs in the modified SFOHNRs/CPE, which showed the highest sensitivity, was chosen as the optimum value for further experiments.

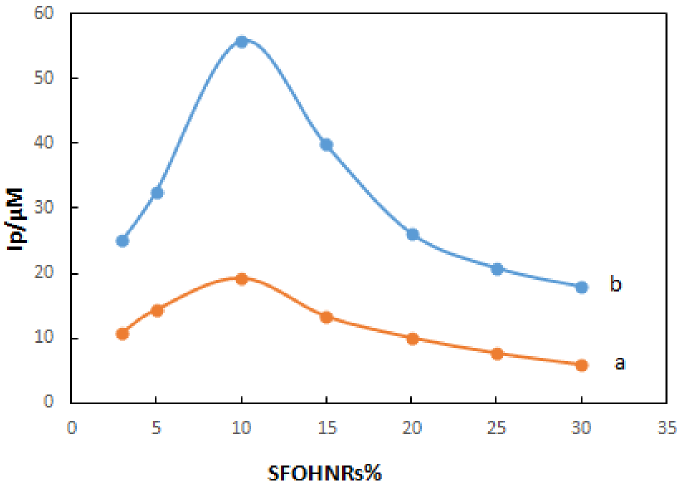

Fig. 1. Effects of percentage of modifier on the oxidation peak currents of 30 µM TRA (a) and 15µM DA(b)

3. RESULTS AND DISCUSSION

3.1. Structural characterization of SFOHNRs

The morphology of SFOHNRs was determined by FESEM and EDX analysis (Fig. 2). Fig. 2A and 2B show the images of SFOHNR in different scales. They indicate that the length and diameter of nanorods are around 1.5 µm and 50-200 nm respectively. Fig. 2C shows map data structure of SFOHNRs which indicate well distribution of constructed atoms in the nano material. The EDX spectrum of SFOHNRs is shown in Fig 2D. The results confirm presence of the Fe, O and Sn in the fabricated SFOHNRs.

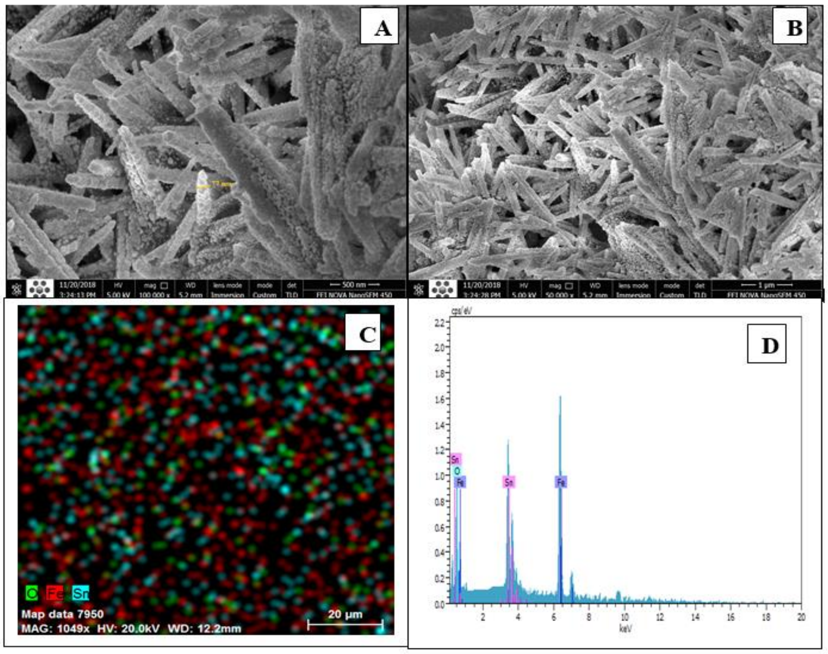

Fig. 2. The FESEM images of SFOHNRs (A,B), Chemical map data of SFOHNRs (C) and EDX spectrum of SFOHNRs (D)

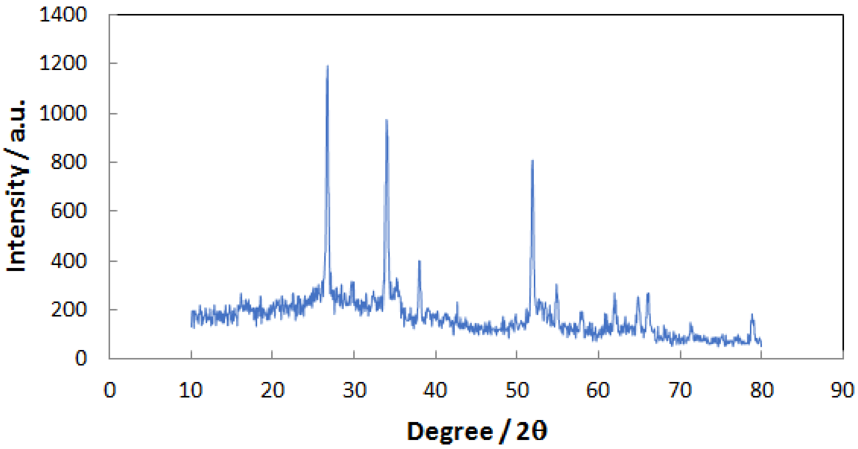

Fig. 3. XRD pattern of the SFOHNRs

The crystal structure and phase composition of the prepared SFOHNRs was also confirmed by XRD measurements (Fig. 3). The dominant peaks are at 2θ values of 26.6 °, 29.6 °, 33. 9, 35.0 °, 37.9 °,41.1 °,51.8 °, 54.55 °,57.8°,61.9°, 64.8 °, 66.0 °,70.2 ^{0}and 78.8 ° which could be indexed to SFOHNRs according to JCPDS No. 33-0664 (for α-Fe_2O_3) and 41-1445 (for SnO_2) similar to those reported previously [39].

3.2. Optimization of experimental parameters

According to the investigation on effect of electrolyte, SFOHNRs /CPE showed the best sensitivity toward determination of DA and TRA in 0.1M Ammonia buffer solution (ABS). Therefore, further electrochemical investigations were obtained in 0.1M ABS. The effect of pH on the electrochemical oxidation of 20 µM DA and 40 µM TRA is shown in Fig. 4A using DPV method. As it can be seen, the oxidation peak currents for both DA and TRA increased from pH5.0 to 8.0 and then decreased with pH changes from 8.0 to 10.0 (Fig. 4B). Consequently, the ABS with a pH of 8.0 was chosen as the optimum value for simultaneous determination of DA and TRA.

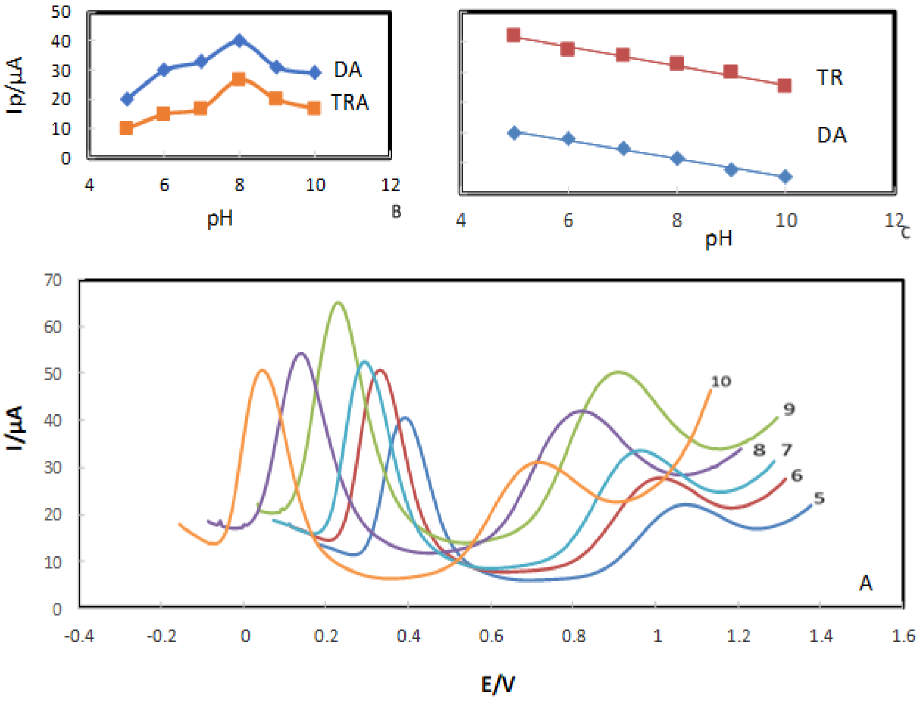

Fig. 4. (A) DPVs of SFOHNRs /CPE in 0.1 M ABS at different pH values in the presence of 20 µM of DA and 40 µM of TRA. Insets: (B) plot of peak currents vs. pH values and (C) plots of E vs. pH.

Fig. 4C shows the relationship between oxidation peak potentials of DA and TRA solutions and pH. The relationships between the E_{pa} and pH were as follows:

E_{pa} (V) =1.3486 - 0.0631pH (R^2=0.9834) TRA (1)

E_{pa} (V) = 0.714 3 - 0.0606 pH (R^2= 0.9939) DA (2)

The fact that the slope of these equations is close to the Nernstian values (0.0592 m/n) which suggests an equal number of electrons (n) and protons (m) involved in the electrochemical oxidations of DA and TRA.

In order to get the highest sensitivity for simultaneous determination of DA and TRA, accumulation time was optimized. The results showed that the anodic peak currents of DA and TRA increased by increasing accumulation time and then leveled off at 40 s. Therefore, accumulation time of 40 s was chosen as the optimum operation parameter for further experiments.

3.3. Electrochemical investigation of DA and TRA at SFOHNRs /CPE

Cyclic voltammetry (CV) experiments of 45µM TRA and 30 µM DA in 0.1 M ABS at SFOHNRs/CPE under optimum conditions was inspected (Fig. 5). As can be seen TRA showed irreversible oxidation peak. However, CV experiments showed reversible redox peaks for DA.

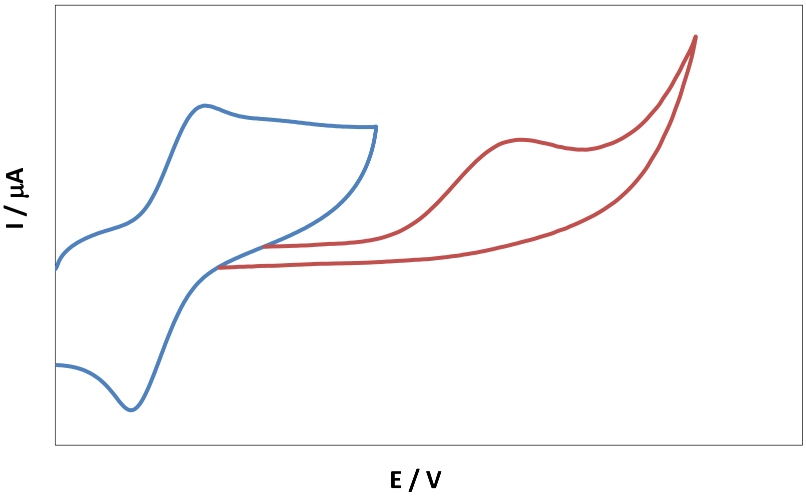

Fig. 5. Cyclic voltammograms of 45µM TRA and 30 µM DA in 0.1 M ABS at SFOHNRs/CPE under optimum conditions at scan rate of 100 mV/s

Figure 6 show differential pulse voltammograms of 20 µM DA and 20 µM TRA at (**a**) CPE, (**b**) SFOHNRs/CPE under optimum conditions. The results show higher oxidation peaks for DA and TRA at SFOHNRs /CPE respect to CPE. In addition, slight shifts of peak potentials toward less positive potentials for DA and TRA were observed at modified electrode. These phenomena might be due to electrocatalytic effect of SFOHNRs. In addition, high surface area of SFOHNRs may leads to higher oxidation peak currents for DA and TRA. Therefore, in this work application of SFOHNRs as the modifier of CPE was considered.

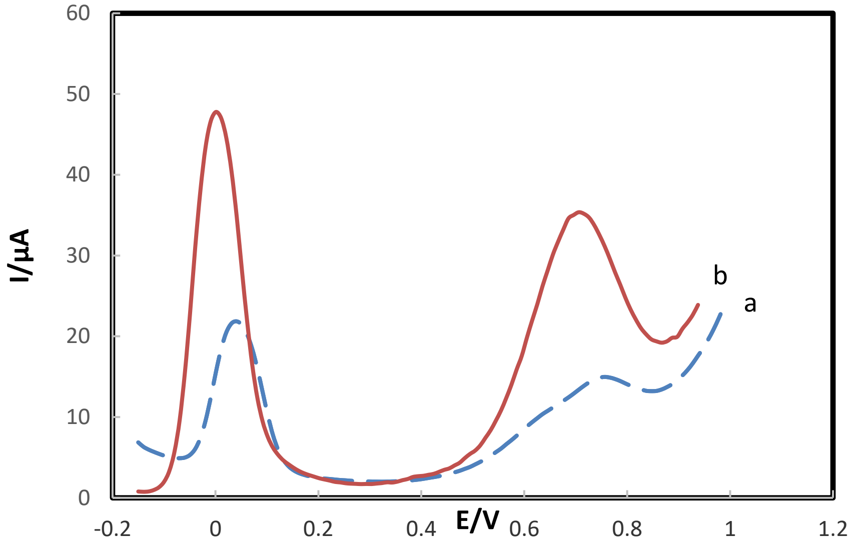

Fig. 6. DPVs of 20 μM of DA and 20 μM of TRA in 0.1 M ABS (pH=8) at (a) CPE and (b) SFOHNRs /CPE

To investigate the effect of the potential scan rate on the oxidation peak potentials and peak currents of DA and TRA at SFOHNRs/CPE in 0.1M ABS (pH=8), CV experiments were carried out under different scan rates varying from 20-800 mV s^{-1}. The results indicated that as the scan rate (ν) increased, the oxidation peak potentials of DA and TRA were shifted to more positive potentials however reduction peak potential of DA shifted to less positive potentials. These phenomena strongly suggest the kinetic limitation of both electrochemical processes.

According to Laviron's theory, for a reversible process, the charge transfer coefficient (α) and electron transfer rate constant (k_s) can be gained by determining the deviation of ΔE_p as a function of log scan rate at scan rates higher than $\frac{200}{n}$ mV s^{-1} using Eqs. (3), (4) and (5) [40].

$$E_{pc} = K - 2.303\ (RT/(\alpha_c)nF)\ \log\ (\nu) \tag{3}$$

$$E_{pa} = K + 2.303\ (RT/\alpha_a nF)\ \log\ (\nu) \tag{4}$$

$$\log k_s=\alpha\log(1-\alpha)+(1-\alpha)\log\alpha-\log(RT/nF\upsilon)-\alpha(1-\alpha)\ (nF\Delta Ep/2.3RT) \tag{5}$$

By considering two electron transfers for oxidation of DA the value of 0.46 for α_c and 0.54 for α_a was obtained. By substituting α value into equation (5), an electron transfer rate constant, $k_s = 2.13\ s^{-1}$, was obtained. According to Laviron's theory, for an irreversible anodic reaction, the relationship between E_p and ν can be obtained as follow:

$$E_p = E^0 - (RT/\alpha_a nF)\ \ln\ (RTK_s/\ \alpha_a nF) + (RT/\alpha_a nF)\ \ln\upsilon \tag{6}$$

According to the slope of the straight line of Ep vs. lnν and by considering value of n equal to 1, value of α for TRA was calculated to be 0.37 at 25^{oC}. Considering Eq. (6) E° can be obtained from the intercept of a plot of the Ep vs. lnv. Finally of k_s value for TRA was calculated as 0.94 s^{-1} by applying value of E^0 and α_a in the Eq. (6). The great value of the electron transfer rate constants showed the high efficiency of the SFOHNRs /CPE to accelerate electron transfer between the DA, TRA and the electrode surface.

3.4. Linear dynamic range and detection limit of the method

DPV technique was used to draw calibration curve for simultaneous determination of DA and TRA under optimum conditions. The solutions were made of various concentrations of DA and TRA in a 0.1M ABS (pH=8) at SFOHNRs /CPE as the working electrode to carry on DPV experiments (Fig. 7).

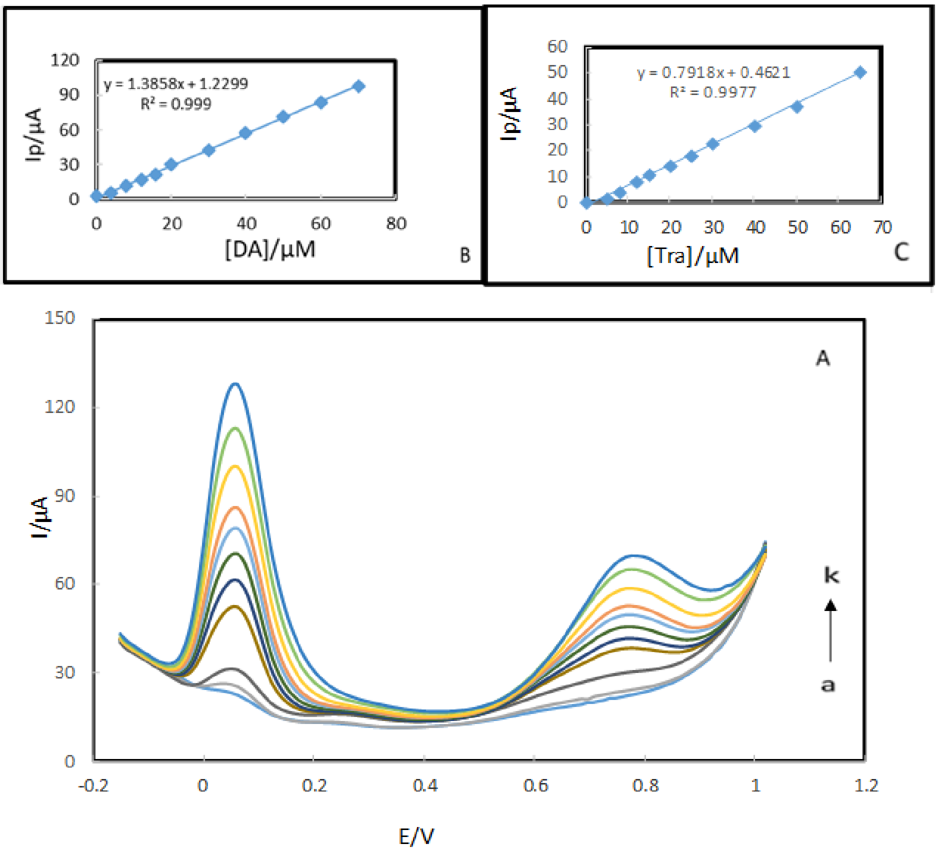

Fig. 7. (A) DPV voltammograms for different concentrations of DA and TRAmixture as (a) 0.1 + 0.5, (b) 0.3 + 0.7, (c) 0.5 + 1, (d) 0.8 + 1.5 (e) 1.5 + 3, (f) 3 + 6, (g) 6 + 12, (h)15 + 30 , (i) 30 + 40,(j) 40+50,(k) 70+65 respectively, in which the first value is the concentration of DA in μM and the second value is the concentration of TRA in μM respectively. Insets: (B) Plot of peak currents as a function of DA concentrations. (C) Plot of the peak currents as a function of TRA concentrations

Fig. 7A shows differential pulse voltammograms of mixture of DA and TRA by synchronous changing their concentrations. The corresponding calibration curves were shown in insets B and C respectively. The results indicated that the corresponding anodic peak currents were proportional to DA and TRA concentrations in the range of 0.1-70 µM and 0.5-65 µM, respectively. The limits of detection (LOD) were obtained to be 40nM and 65 nM (S/N = 3) for DA and TRA, respectively.

3.5. CA measurements

Useful information including diffusion coefficient (D) of DA and TRA at SFOHNRs/CPE can be obtained from CA method (Fig.8). To perform CA determination, the potential of the modified electrode was separately adjusted to 320 mV and 700 mV for DA (Fig. 8A) and TRA (Fig. 8B), respectively. The analysis of CA data is based on the Cottrell equation, which defines the current-time dependence for linear diffusion control. Cottrell equation is described by the following equation:

$$I= nFAD^{1/2}C\pi^{-1/2}t^{-1/2} \tag{7}$$

According to this equation, a plot of I vs. $t^{-1/2}$ is linear in diffusion-controlled situations (mass transport). Therefore, the value of D can be found from its slope.

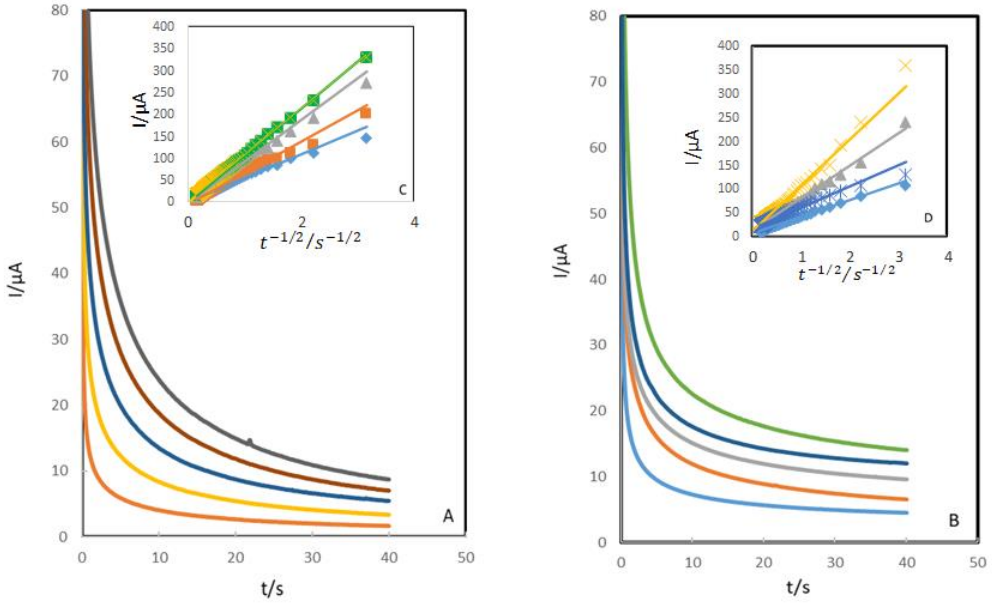

Fig. 8. (A) Chronoamperograms were obtained in the presence of 0.1,0.2, 0.3 0.4 and 0.5 mM of DA at SFOHNRs/CPE in 0.1 M ABS (pH =8). (B) Chronoamperograms were obtained in the presence of 0.1,0.2, 0.3, 0.4 and 0.5 mM of TRA at SFOHNRs /CPE in 0.1 M ABS (pH =8). Insets(C) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms in (A) for DA and (D) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms in (B) for TRA

The plots of I vs. $t^{-1/2}$ were plotted in Fig. 8C for DA and in Fig.8D for TRA. Finally, the mean values of D were obtained to be 4.54 $\mu cm^2\ s^{-1}$ and 2.12$\mu cm^2\ s^{-1}$ for DA and TRA, respectively.

3.6. Stability and repeatability of FSONFs /CPE

The stability of SFOHNRs/CPE was evaluated at dry and wet conditions during certain time intervals by repetitive DPV measurements. The measuring solution includes 20 µM of DA and 40 µM TRA in 0.1M of ABS with pH of 8 and the storage solution was contained only ABS (0.1M) with the same pH. Under wet condition, when the modified electrode was subjected to an experiment every 30 min up to ten hours, the corresponding oxidation peak current for DA and TRA were decreased only 1.5% and 3%, respectively. However, when the electrode was stored in the atmosphere for 10 days (dry condition), the oxidation peak currents of DA and TRA in the solution were reduced less than5.8% and9.4 %, respectively. These results confirm high stability of the sensor under wet and dry conditions. The repeatability of the sensor was measured by 8 consecutive determinations of the 20 µM DA and 40 µM TRA using DPV method. The measured RSDs for DA and TRA were obtained as 1.6% and 2.9 % respectively. These small values point out that the electrode was stable during continuous voltammetric measurements, and it was not affected by surface fouling.

3.7. Interference studies of the method

To investigate selectivity of the proposed method, the effect of some probable interfering species was evaluated in 40 µM DA and 60 µM TRA solutions under the optimum conditions using DPV technique. The tolerance limit for each potential interfering species was taken as the maximum concentration of other species as interferent which gives an error of $\leq$ 5% in the determination of DA or TRA. The results are shown in Table 1. The results indicated that interfering species did not significantly influence the peak currents for DA and TRA which confirm good selectivity of the sensor.

3.8. Real sample analysis

Human urine and blood serum were chosen to investigate the applicability of the presented method in simultaneous determination of DA and TRA in the real samples using DPV method. The prepared real samples were spiked with appropriate amounts of DA and TRA samples and their corresponding oxidation peak potential were obtained under optimum conditions. Concentrations were obtained using standard additions method to reduce any probable matrix effect. The results are shown in Table 2 and Table 3. The good recoveries verify that the proposed modified electrode has potential to apply for simultaneous determination of DA and

TRA in biological systems, without need any special pretreatments and using time consuming analysis time.

Table 1. Maximum tolerable concentration of interfering species

Interfering species	DA $C_{int^*}/(\mu M)$	TRA $C_{int}/(\mu M)$
Tyrosin	1300	2600
L-histidine	1300	1200
Uric acid	400	300
Ascorbic acid	800	500
L-glutamic acid	1600	1800
Histidine	1100	350
Tryptophan	900	1000
L-alanin	1200	3700
Aspartic acid	400	1800

*C_{int} refers to interfering compound concentration

Table 2. Estimation of DA and TRA in human serum

Spiked (μM)		**Found[a]**		**R.S.D. (%)**		**Recovery (%)**	
DA	TRA	DA	TRA	DA	TRA	DA	TRA
0	0	<DL	<DL	-	-	-	-
5.0	20.0	4.8	19.2	1.6	1.9	96.0	98.5
15.0	30.0	15.3	29.5	1.3	1.5	102.0	98.3

[a]Average of five determinations at optimum conditions

Table 3. Estimation of DA and TRA in human urine sample

Spiked (μM)		**Found[a]**		**R.S.D. (%)**		**Recovery (%)**	
DA	TRA	DA	TRA	DA	TRA	DA	TRA
0	0	<DL	<DL	-	-	-	-
5.0	20.0	5.2	19.8	1.4	1.5	104.0	99.0
15.0	30.0	14.7	29.6	1.6	1.3	98.0	98.6

[a]Average of five determinations at optimum conditions

4. CONCLUSION

In this work application of a novel sensor based on SFOHNRs modified carbon paste electrode (SFOHNRs /CPE) is introduced. The fabricated sensor for the first time was used for simultaneous electrochemical determination of DA and TRA. The presence of SFOHNRs leads to excellent sensitivity of the proposed sensor for simultaneous determination of DA and TRA. The electrode also showed high stability and good repeatability in repetitive experiments. The interfering study of some species showed no significant interference with determination of DA and TRA. Application of the proposed sensor for the determination of DA and TRA in some real samples gave satisfactory results, without the necessity of sample pretreatments or time-consuming extractions. The simple fabrication procedure, high speed, reproducibility, high stability, wide linear dynamic range, low detection limit and high sensitivity, suggest that the proposed sensor is an attractive candidate for practical applications. There are no conflicts to declare.

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