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Full Paper

$NiFe_2O_4$ Nanoparticles Modified Screen Printed Electrode for Simultaneous Determination of Serotonin and Norepinephrine

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Abstract- $NiFe_2O_4$ nanoparticles were successfully applied at a screen printed electrode ($NiFe_2O_4$/SPE). At first, $NiFe_2O_4$ nanoparticles were deposited on the SPE. This new modified electrode system was characterized by cyclic voltammetry (CV), chronoamperometry (CHA) and differential pulse voltammetry (DPV). $NiFe_2O_4$/SPE was used for simultaneous determination of serotonin and norepinephrine. It was observed that an electrode with electrochemical deposited of $NiFe_2O_4$ nanoparticles has higher electrocatalytic activity for the oxidation of serotonin. Differential pulse voltammetry exhibited a linear dynamic range over the concentration range of 0.1-300.0 μM and a detection limit (3σ) of 0.07 μM for serotonin in the optimum conditions. Finally, DPV was used for simultaneous determination of serotonin and norepinephrine and their detection real samples.

Keywords- $NiFe_2O_4$ nanoparticles, Serotonin, Norepinephrine, Screen printed electrode, Electrocatalysis

1. INTRODUCTION

Norepinephrine (NE) which is existing in the nervous systems and biological body fluids is an important biochemical carrier in mammalian central nervous system [1-3]. It is released as a metabotropic neurotransmitter from nerve endings in the sympathetic nervous system and some areas of the cerebral cortex. It is used to treat myocardial infarction hypertension, bronchial asthma and organic heart disease [4]. Extremely abnormal concentration levels of norepinephrine may lead to the occurrence of many diseases, such as ganglion neuronal, ganglia neuroblastoma, paraganglioma and Parkinson' disease [5,6]. In these cases, it is very necessary to develop fast, accurate and sensitive methods for the quantitative determination of norepinephrine in biological fluids including urine and blood samples [7-9].

Serotonin or 5-hydroxytryptamine (5-HT), is one of the monoamine neurotransmitters widely distributed in our body and synthesized in brain, intestine, and spinal cord. It plays a vital role in the regulation of numerous behavioral and physiological functions such as mood, sleep, emesis, sexuality, and appetite. Low level of serotonin is associated with several diseases and disorders, including depression, anxiety, migraines, unregulated hemostasis, blood clotting, sudden infant death syndrome and carcinoid syndrome. On the other hand, high levels of serotonin can cause noticeable toxicity and potentially fatal effects known as serotonin syndrome [10-17]. Therefore a suitable selective, simple, inexpensive, fast, sensitive and accurate detection method is required for determining norepinephrine and serotonin.

Electroanalytical methods have been proven to be rapid, simple and sensitive and have an impact in the most of fields of science, for example clinical diagnostics, food quality control, security and environmental analysis [18-31]. A general method of preparation of electroanalytical devices consists the bulk or surface modification of the electrode with species enabling chemical or biological recognition. Therefore, the choice of a suitable electrode is important in electroanalytical research processes. Biocompatibility and capability to incorporate chemical species without their loss in operating medium are of greatest importance [32-53].

Magnetic nanoparticles are of the most popular materials in analytical biochemistry, medicine, removal of heavy metals and biotechnology, and have been increasingly applied to immobilize proteins, enzymes, and other bioactive agents due to their unique advantages. $NiFe_2O_4$ nanoparticles ($NiFe_2O_4$ NPs) have attracted an increasing interest in construction of sensors and biosensors because of their good biocompatibility, strong super paramagnetic property, low toxicity, easy preparation and high adsorption ability. $NiFe_2O_4$ with an inverse spinel structure shows ferrimagnetism that originates from magnetic moment of anti-parallel spins between Fe^{3+} ions at tetrahedral sites and Ni^{2+} ions at octahedral sites. Moreover, $NiFe_2O_4$ NPs exhibit high surface area and low mass transfer resistance [54-56].

In the present study, a novel electrode system was fabricated using a SPE modified by $NiFe_2O_4$ nanoparticles. This is a novel electrode system, which used for the first time for determination of serotonin and norepinephrine. This modified electrode was quite effective not only to detect serotonin, but also in simultaneous determination of serotonin and norepinephrine in mixture. Detection limit and linear range for serotonin in this work are comparable with other researches.

2. EXPERIMENTAL

2.1. Apparatus and chemicals

A Perkin Elmer BX FT-IR infrared spectrometer was used to record Fourier transform infrared (FT-IR) spectra in transmission mode. The range 400-4000 cm^{-1} was considered to record FT-IR spectra for the purpose of examining the type of resulting chemical bonds. In order to verify products' formation, X-ray powder diffraction (XRD) analysis was carried out on a Philips PC-APD X-ray diffractometer including graphite monochromatic CuKα radiation (α_1,λ_1=1.54056 Å, α_2,λ_2=1.54439 Å). Joint Committee on Powder Diffraction Standards (JCPDS) card was implemented to index the X-ray diffraction pattern. JSM 6389 LV with EDX microanalysis was utilized to collect the samples' SEM images.

An Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands) was utilized to conduct electrochemical measurements. The General Purpose Electrochemical System (GPES) software was used to control the defined experimental settings. A graphite working electrode, a silver pseudo reference electrode and a graphite counter electrode are the parts that form the screen printed electrode (DropSens, DRP-110, Spain). In order to take PH measurements, a 710 pH meter metrohm was used.

Analytical grade serotonin and norepinephrine were used along with all other analytical grade reagents which were obtained from Merck, Darmstadt, Germany. Orthophosphoric acid was used to prepare buffer solution. The relevant salts were above 2.0-9.0 pH range.

2.2. Synthesis of $NiFe_2O_4$ nanoparticles

A hydro/solvothermal approach was implemented with the presence of urea for the aim of synthesizing $NiFe_2O_4$ nanoparticles. A 60 ml solution of deionized water was used to dissolve a urea solution prior to adding a 20 ml of polyethylene glycol (PEG) which resulted in the formation of brown homogeneous solutions. Subsequently, 10 mL $FeCl_3.6H_2O$ (16 mmol) and 10 mL $NiCl_2.6H_2O$ (8 mmol) were then added to the solution respectively. The resulting solution, with urea/Fe^{3+} stoichiometric 30 molar ration including a surplus of urea that creates adequate precipitating ions to form metal oxides, were mixed magnetically until the solution was completely dissolved at 25 °C. The mentioned solutions were additionally homogenized for a period of 15 min in an ultrasonic bath prior to being relocated into a Teflon-lined

stainless steel autoclave with 200 ml capacity for the purpose of conserving them for a 24 h time period in an oven at 200 °C. The resultant precipitates were then centrifuged. Upon centrifugation, deionized water and absolute ethanol was applied repeatedly to get rid of product impurities. The final product was dried for 12 h in a vacuum oven set at 70 °C.

2.3. Preparation of the electrode

$NiFe_2O_4$ nanoparticles were used to coat the bare screen electrode as presented below. Upon the dispersion of 1 mg of $NiFe_2O_4$ nanoparticles with ultrasonication for an hour, a stock $NiFe_2O_4$ nanoparticles solution in 1 ml aqueous solution was arranged while while 2 µl of aliquots of the $NiFe_2O_4/H_2O$ suspension solution was applied on the carbon working electrodes. The solvent was then left to evaporate at room temperature.

2.4. Preparation of real samples

One milliliter of a norepinephrine ampoule (Darou Pakhsh Co. Tehran, Iran, contained 4 mg in 4 ml of norepinephrine) was diluted to 10 mL with 0.1 M PBS (pH 7.0); then, different volume of the diluted solution was transferred into each of a series of 25 mL volumetric flasks and diluted to the mark with PBS. The serotonin and norepinephrine contents were analyzed by the proposed method using the standard addition method.

Upon collecting urine samples, they were promptly kept in a refrigerator. 15 min at 2000 rpm centrifugation was implemented for 10 ml of the samples. A 0.45 µm filter was used to filter the supernatant. Then, various solution volumes were put into a 25 ml volumetric flask prior to being diluted with PBS of pH 7.0 to the mark. Various volumes of serotonin and norepinephrine were used to spike the diluted urine samples. The proposed method was used to analyse the serotonin and norepinephrine contents via the standard addition method.

3. RESULT AND DISCUSSION

3.1. Morphology and structure of $NiFe_2O_4$ nanoparticles

The vibration frequencies in the infrared spectrum of a molecule were considered to be a unique physical property and were a characteristic of the molecule. Fig. 1 shows two persistent absorption bands corresponding to the vibration of tetrahedral and octahedral complexes at 599 cm^{-1} and 465 cm^{-1}, respectively. Those bands confirmed the formation of spinel nickel ferrite structure. As can be seen from FT-IR spectra the normal mode of vibration of tetrahedral cluster (599 cm^{-1}) is higher than that of octahedral cluster (465 cm^{-1}). This is due to the shorter bond length of tetrahedral cluster than the octahedral cluster [54,55].

An XRD spectrum of the $NiFe_2O_4$ nanoparticles is shown in Fig. 2. For the $NiFe_2O_4$ nanoparticles, the eleven characteristic peaks occur at 2θ of 30.48°, 35.87°, 36.21°, 45.52°, 51.89°, 57.51°, 63.63°, 72.14°, 75.52°, 76.68°, and 79.68°, which are marked by their corresponding indices (220), (311), (222), (400), (422), (511), (440), (620), (533), (622) and (444), respectively. This reveals that the magnetic particles are pure $NiFe_2O_4$ with a spinel structure. No diffraction peaks of other impurities such as α-Fe_2O_3 or NiO were observed. The broadness of the diffraction peaks suggests the nano-sized nature of the product and the average crystallite size (t) of it was calculated using the Debye–Scherrer formula as 40.0 nm. $t=0.9\ \lambda / \beta \cos(\theta)$ where λ is the wavelength of the X-ray radiation (1.54056 Å for Cu lamp), θ is the diffraction angle and β is the full width at half-maximum (FWHM) [56].

The morphology of the product was examined by SEM. Fig. 3A depicts the SEM pictures of $NiFe_2O_4$ nanoparticles. From the graph, it was observed that the nanoparticles, which are nearly spherical, are not agglomerated and they are seen as less than 10 nm.

The EDX analysis was performed to further confirm the composition of the obtained products. Fig. 3B shows that the products are composed of Ni, Fe and O. The C peak in the spectrum is attributed to the electric latex of the SEM sample holder.

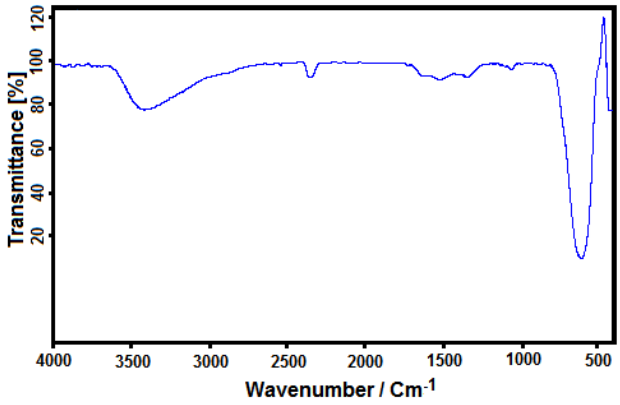


Fig. 1. FT-IR spectra of $NiFe_2O_4$ nanoparticles

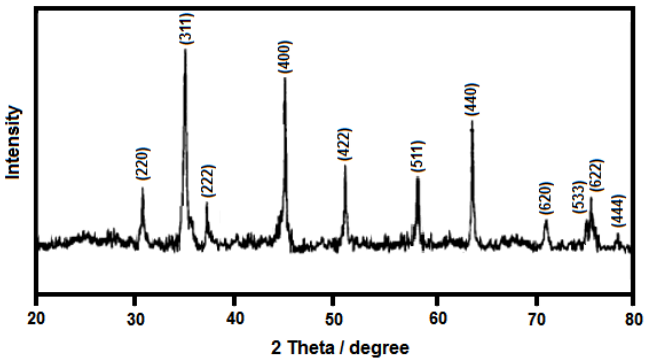


Fig. 2. X-ray diffraction patterns of the $NiFe_2O_4$ nanoparticles

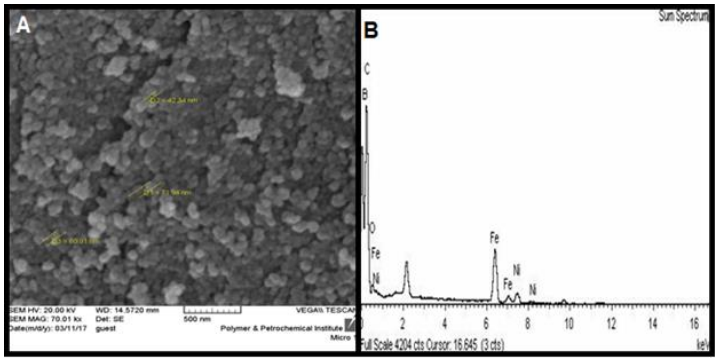
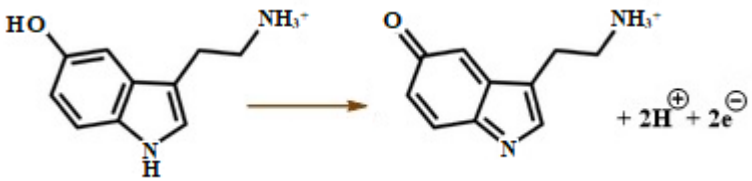


Fig. 3. (A) SEM micrographs with (B) its EDX spectra of $NiFe_2O_4$ nanoparticles

3.2. Electrochemical behaviour of serotonin at the surface of various electrodes

Serotonin electrochemical activities are dependent on the aqueous solution's pH value (Scheme 1). Thus, the solution pH optimization is vital to acquire favorable results for serotonin electro-oxidation. Moreover, serotonin electrochemical behavior was examined via a 0.1 M phosphate buffer solution (PBS) in various pH values in the 2.0-9.0 range by voltammetry at $NiFe_2O_4$/SPE surface. Results indicated that serotonin electro-oxidation at $NiFe_2O_4$/SPE surface is more favourable under neutral circumstances compared to acidic or basic medium state. The optimal pH for serotonin at was selected at pH 7.0 at $NiFe_2O_4$/SPE surface. Serotonin oxidation at the $NiFe_2O_4$/SPE (Curve a) and unmodified SPE (Curve b) are illustrated in Fig. 4. Because of serotonin oxidation, that is approximately 50 mV more negative compared to the unmodified SPE, the peak potential happens at 450 mV. Furthermore, regarding serotonin oxidation, $NiFe_2O_4$/SPE exhibits more anodic peak current in comparison to unmodified SPE which is a sign that unmodified SPE modification with $NiFe_2O_4$ nanoparticles has considerably enhanced electrode performance towards serotonin oxidation.



Scheme 1. Electro-oxidation mechanism of serotonin at $NiFe_2O_4$ nanoparticles modified electrode

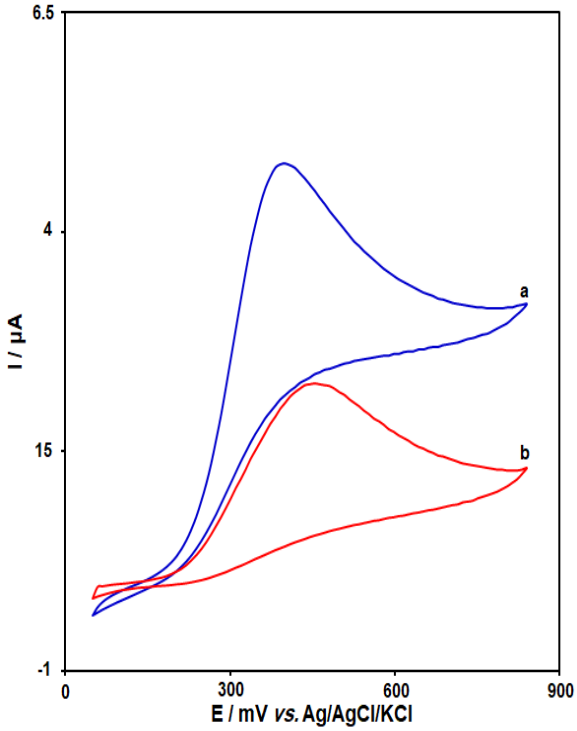


Fig. 4. CVs of $NiFe_2O_4$/SPE (a) and unmodified SPE (b) in 0.1 M PBS (pH 7.0) containing 100.0 µM serotonin. In all cases the scan rate was 50 mV s^{-1}

3.3. Effect of scan rate on the results

Increasing the scan rate resulted in enhanced oxidation peak current according to the results obtained from the study of the effect of potential scan rates on the oxidation currents of serotonin, Fig. 5. Moreover, a linear relationship was observed between I_p and the square root of the potential scan rate ($v^{1/2}$) which confirm that the oxidation process of analyte is under the control of diffusion.

The Tafel curve for the serotonin was plotted according to the data acquired from the Tafel regions (rising segments) taken from current–voltage curve obtained at 10 mVs^{-1} (Fig. 6). The Tafel regions in the current-potential curve are affected by the kinetics of electron transfer in the electrode reaction. The Tafel slope was obtained 0.1361 V which indicates that in the electrode process, there is an electron rate determining step (RDS) with charge transfer coefficient (α) of 0.57 [57].

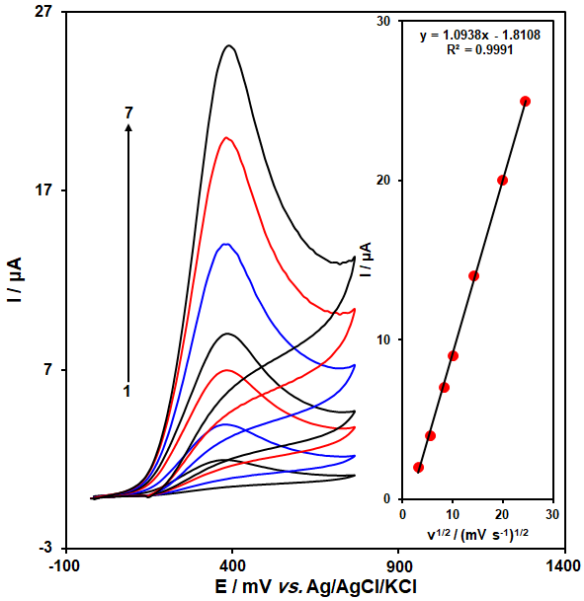


Fig. 5. CVs of $NiFe_2O_4$/SPE in 0.1 M PBS (pH 7.0) containing 20.0 µM serotonin at various scan rates; 10, 30, 70, 100, 200, 400 and 600 mV s^{-1}. Inset: Variation of anodic peak current *vs*. $v^{1/2}$

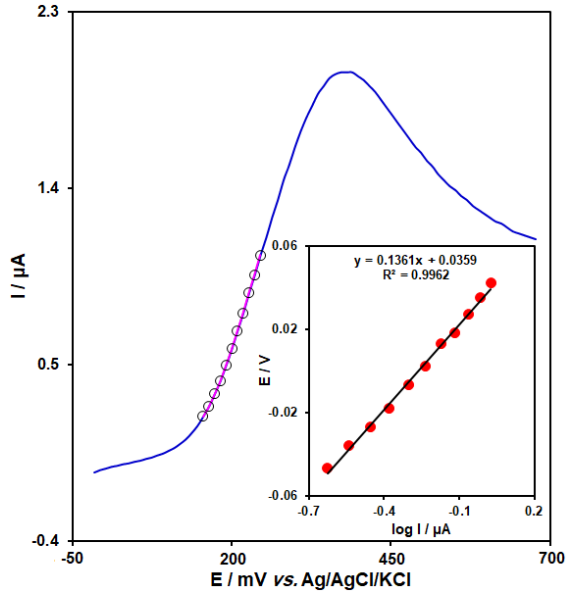


Fig. 6. LSV (at 10 mV s^{-1}) of electrode in 0.1 M PBS (pH 7.0) containing 20.0 µM serotonin. The points are the data used in the Tafel plot. The inset shows the Tafel plot derived from the LSV

3.4. Chronoamperometric analysis

The analysis of chronoamperometry for serotonin samples was performed by use of $NiFe_2O_4$/SPE *vs*. Ag/AgCl/KCl (3.0 M) at 450 mV. The Chronoamperometric results of

different concentrations of serotonin sample in PBS (pH 7.0) are depicted in Fig. 7. The Cottrell equation is used for chronoamperometric analysis of electroactive moieties under the mass transfer limited conditions as follow [57]:

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

Where D and C_b represents the diffusion coefficient ($cm^2\ s^{-1}$) and the bulk concentration (mol cm^{-3}), respectively. The plot of I *vs.* $t^{-1/2}$ was obtained based on experimental results as shown in Fig. 7A, with the best fits for different concentrations of serotonin. The resulted slopes of the straight lines in Fig. 7A, were then plotted versus the concentration of serotonin (Fig. 7B). Finally, according to the resulting slope of the 7B plot and Cottrell equation, the mean value of D was determined to be 3.4×10^{-6} cm^2/s.

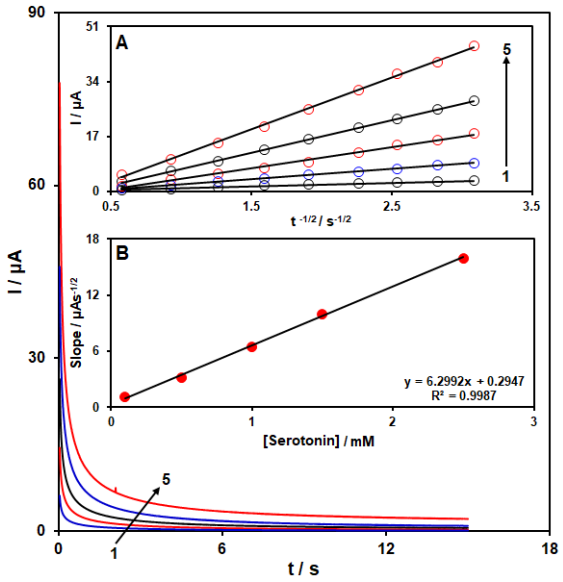


Fig. 7. Chronoamperograms obtained at $NiFe_2O_4$/SPE in 0.1 M PBS (pH 7.0) for different concentrations of serotonin (0.1, 0.5, 1.0, 1.5 and 2.5 mM). Insets: (A) Plots of I *vs.* $t^{-1/2}$ obtained from chronoamperograms 1-5. (B) Plot of the slope of the straight lines against serotonin concentration

3.5. Calibration curves

The quantitative analysis of serotonin was carried out in aqueous solution according to the resulting peak currents of serotonin on the surface of $NiFe_2O_4$/SPE. The modified electrode ($NiFe_2O_4$/SPE) was employed in differential pulse voltammetry (DPV) as working electrode over the concentration range of serotonin in 0.1 M (Fig. 8) (Step potential=0.01 V and pulse amplitude=0.025 V). The DPV analysis offers advantages including higher sensitivity and better performance in analytical applications. The DPV results revealed that

within the serotonin concentration range from 0.1 to 300.0 µM there is a linear relation with the peak currents. The correlation coefficient and the detection limit were obtained 0.9993 and 0.07 µM, respectively. Table 1. shows a comparison of the analytical figures of merit of the proposed method with electrochemical techniques for the determination of serotonin.

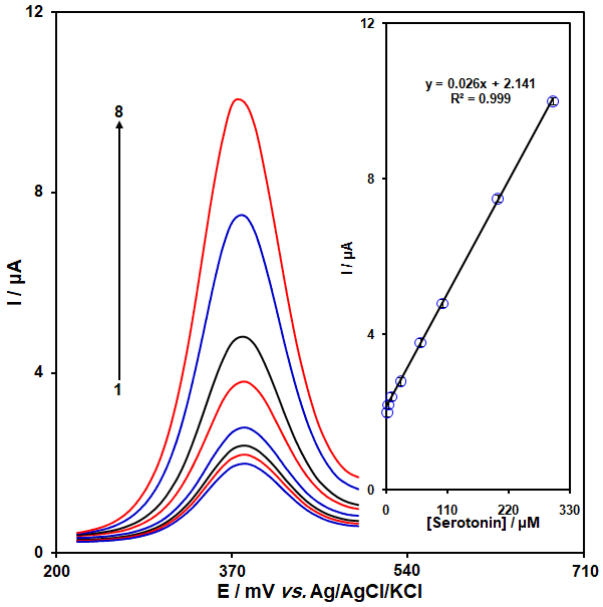


Fig. 8. DPVs of $NiFe_2O_4$/SPE in 0.1 M PBS (pH 7.0) containing different concentrations of serotonin (0.1, 2.5, 7.5, 25.0, 60.0, 100.0, 200.0 and 300.0 µM). Inset: Plot of I *vs.* serotonin concentrations

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

Electrode	**Modifier**	**LOD (µM)**	**LDR (µM)**	**Ref.**
Glassy carbon	Carbon nanotube-TiO_2/ionic liquid	0. 1	0.1-650.0	[58]
Screen printed	Single-walled carbon nanotubes	0.4	1.0-250.0	[59]
Screen printed	multi-walled carbon nanotubes -SiO_2-chitosan composites	0.01	0.1-20.0	[60]
Pt	Poly (3, 4-ethylene dioxythiophene) /Carbon nanotube	0.7	1.0-100.0	[61]
Screen printed	$NiFe_2O_4$ Nanoparticles	0.07	0.1-300.0	This work

3.6. Simultaneous determination of serotonin and norepinephrine

The electrochemical determination of serotonin using bare electrodes suffers from interference by norepinephrine, because the oxidation potential for norepinephrine is fairly close to that of serotonin. The determination of two compounds was performed by simultaneously changing the concentrations of serotonin and norepinephrine, and recording the DPVs (Fig. 9). The voltammetric results showed well-defined anodic peaks at potentials of 180 and 400 mV, corresponding to the oxidation of serotonin and norepinephrine, respectively, indicating that simultaneous determination of these compounds is feasible at the $NiFe_2O_4$/SPE as shown in Fig. 9.

The sensitivity of the modified electrode towards the oxidation of serotonin was found to be 0.026 µA μM^{-1}. This is very close to the value obtained in the absence of norepinephrine (0.0264 µA μM^{-1}, see Section 3.4), indicating that the oxidation processes of these compounds at the $NiFe_2O_4$/SPE are independent and therefore, simultaneous determination of their mixtures is possible without significant interferences.

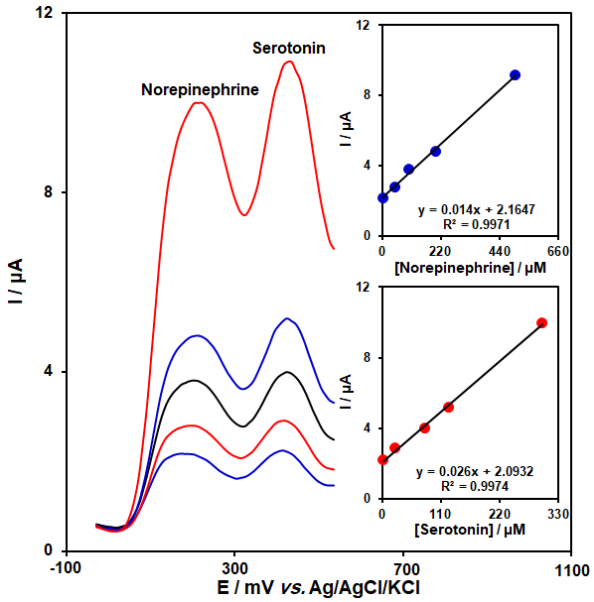


Fig. 9. DPVs of $NiFe_2O_4$/SPE in 0.1 M PBS (pH 7.0) containing different concentrations of norepinephrine and serotonin in µM, from inner to outer: 2.5+2.5, 50.0+25.0, 100.0+80.0, 200.0+125.0 and 500.0+300.0 respectively. Insets (A) plots of I_p *vs.* norepinephrine concentration and (B) plot of I_p *vs.* serotonin concentrations

3.7. Analysis of real samples

To evaluate the applicability of this modified sensor in the analysis of real samples, the proposed method was applied for the serotonin and norepinephrine determination in

norepinephrine ampoule and urine samples. Using the standard addition method, this investigation was performed and the results are given in Table 2. The analysis results of real samples were quite satisfactory for serotonin and norepinephrine recovery. In addition, the mean relative standard deviation (R.S.D.) confirmed the reproducibility of the results.

Table 2. Determination of serotonin and norepinephrine in norepinephrine ampoule and urine samples. All the concentrations are in μM (n=5)

Sample	Spiked		Found		Recovery (%)		R.S.D. (%)	
	Serotonin	Norepinephrine	Serotonin	Norepinephrine	Serotonin	Norepinephrine	Serotonin	Norepinephrine
Norepinephrine ampoule	-	0	-	5.5	-	-	-	1.7
	5.0	7.5	5.1	12.9	102.0	99.2	2.8	3.3
	10.0	12.5	10.1	18.3	101.0	101.6	1.9	2.1
	15.0	17.5	14.8	23.1	98.6	100.4	3.1	2.6
	20.0	22.5	20.3	27.4	101.5	97.8	2.7	2.4
Urine	0	0	-	-	-	-	-	-
	12.0	10.0	12.1	9.9	100.8	99.0	2.9	1.9
	18.0	16.0	17.8	15.9	98.8	99.3	2.2	3.1
	24.0	22.0	24.3	22.3	101.2	101.3	1.8	2.5
	30.0	28.0	29.7	28.6	99.0	102.1	3.3	2.6

3.8. The repeatability and stability of $NiFe_2O_4$/SPE

To study the long-term stability of the $NiFe_2O_4$/SPE, its performance was assessed over a 3-week period. For this purpose, the experiments were repeated after the modified electrode had been stored at room temperature for 2-weeks. As cyclic voltammograms demonstrated, no tangible change was observed in the peak potential of serotonin oxidation except for a drop less than 2.6% compared with initial response. The antifouling capacity of the modified electrode towards oxidation of serotonin and its corresponding oxidation products were investigated by CV analysis.

Voltammograms were recorded in the presence of serotonin after cycling the potential 25 times at a scan rate of 50 mV s^{-1}. According to the results, the peak potentials remained unchanged except a decrement less than 2.2%. These results confirmed that the modified $NiFe_2O_4$/SPE offers higher sensitivity and reduced fouling effect towards serotonin and its oxidation products.

4. CONCLUSION

In the present paper, a SPE was modified with $NiFe_2O_4$ nanoparticles. The electrochemical behavior of the $NiFe_2O_4$/SPE was studied by CV. The modified electrode was used for the electro-oxidation determination of serotonin and norepinephrine. Good sensetivity and reproducibility of the voltammetric responses and low detection limit (0.07 μM), together with the ease of preparation makes the proposed modified electrode very useful for accurate determination of serotonin and norepinephrine in real samples

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