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Development of a new paper based nano-biosensor based on the co-catalytic effect of tyrosinase from banana peel tissue (*Musa Cavendish*) and functionalized silica nanoparticles for voltammetric determination of L-tyrosine

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Abstract

A new and facile method for electrochemical determination of L-tyrosine was designed. Tyrosinase from banana peel tissue was immobilized at fiber matrices of the paper disc via physical adsorption. The mediator potassium hexacyanoferrate and 3-mercaptopropyl trimethoxysilane-functionalized silica nanoparticles were added to the paper disc, respectively. The modified paper disc was placed on the top of the graphite screen printed electrode and electrochemical characterization of this biosensor was studied by cyclic voltammetry and electrochemical impedance spectroscopy methods. The effective parameters like pH, banana peel tissue percentage and amount of mediator loading were optimized. L-tyrosine measurements were done by differential pulse voltammetry with a little sample (3µL) for analysis. The biosensor showed a linear response for L-tyrosine in the wide concentration range of 0.05-600 µM and a low detection limit about 0.02 µM because of co-catalytic effect of enzyme and nanoparticles. The stability of the biosensor and its selectivity were evaluated. This biosensor was applied for the voltammetric determination of L-tyrosine in the blood plasma sample. The results of the practical application study were comparable with the standard method (HPLC). In conclusion, a simple, inexpensive, rapid, sensitive and selective technique was successfully applied to L-tyrosine analysis of the little samples.

Keywords: Tissue biosensor; Tyrosinase; L-tyrosine; Paper based biosensor; Functionalized silica nanoparticles

1. Introduction

L-tyrosine is known as conditionally essential amino acid, synthesized in our body by hydroxylation of L-phenylalanine. The hydroxylation can be limited due to deficiency of phenylalanine hydroxylase. L-tyrosine is a vital constituent of proteins and establishing of a positive nitrogen balance and then, must be supplied in our diet [1, 2]. L-tyrosine is the precursor for L-dopa, dopamine, thyroxin, nor-adrenaline and adrenaline as the hormone [3]. Normal plasma L-tyrosine concentrations have ranged from 30 to 120 μM [4]. Abnormal levels of L-tyrosine in human body lead to many diseases. Low amounts of this amino acid may cause to psychological diseases, such as hypochondria, depression, physical and mental exhaustion [5], and the absence of L-tyrosine may cause to albinism and alkaptonuria [6]. On the other hand, elevated blood L-tyrosine which is happened due to deficiencies in specific enzymes in the L-tyrosine catabolic pathway like tyrosine amino transferase caused to tyrosinemia (HT) types 1, 2, 3, and hypertyrosinema [7, 8]. Therefore, determination of L-tyrosine in the human body is necessary and its content directly indicates the healthy status of the body [9, 10].

Several methods have been reported to the determination of L-tyrosine, such as fluorimetric methods [11], chemiluminescence [12], spectrometric analysis [13], capillary electrophoresis [14], liquid chromatographic–tandem mass spectrometry (LC–MS) [15] and high performance liquid chromatography (HPLC) method [16, 17]. These methods have some disadvantages, such as large material consumption, time consuming and expensive equipment. Electrochemical determination of L-tyrosine by Tyrosinase (Tyr, EC 1.14.18.1) enzymatic activity has been developed, recently [18]. Tyr as polyphenol oxidase catalyzes the oxidation of hydroxyl phenols, like L-tyrosine, to their quinone derivatives. Tyr has been applied in biosensors due to catalysis property [19], inhibition enzyme property [20] and its biomarker activity [21]. This enzyme catalyzes two distinct reactions, which is including hydroxylation of monophenols to *o*–

dihydroxy phenols that is continued by oxidation of *o*–dihydroxy compounds to *o*-quinones. *O*-quinones can be polymerized to melanin brown pigment [22]. likewise, a new mesoporous carbon-containing voltammetric biosensor by Tyr was developed to determine the tyramine in food products [23].

However, using pure enzymes could be one of the limitation of these methods, due to relatively high expense and time consuming process of purification as well as small stability of distinct enzymes [24]. Application of plants tissue instead of distinct enzymes is a strategy that presents sensitive, rapid, cheap and easy method for analysis. For example, Coconut fiber tissue was applied to electrochemical biosensing of hydrogen peroxide [25]. Electrochemical dopamine determination was done by a new banana tissue-MWCNTs modified carbon paste electrode [26]. Banana peel tissue as a real source of polyphenol oxidase [27], was applied in the current study. Several methods have been used for immobilization of raw plant tissues, that in this work we applied a new method, using of paper as immobilization matrices via physical adsorption. The paper based biosensor has some advantage, including inexpensive, light, disposable, biodegradable and easy to use [28]. Furthermore, this method requires a little sample for analysis.

The mediators such as quinones, organic dyes, hexacyanoferrate, ferrocene and its derivatives have been applied in different biosensors for shuttle electrons between the redox center of the enzyme and the electrode surface [29]. In this research we have used potassium hexacyanoferrate as mediator (M) for the better electrical communication between the embedded redox center of the Tyr and the surface of screen printed electrode (SPE).

So far, new substance nanostructures for fabrication of biosensors has been developed because of their considerable ability in the fast electron transfer, large surface area, powerful electrical conductivity, strong mechanical strength and high mechanical stability [30]. The paper

based nanobiosensors have some advantages, such as stability, higher lifetime and bringing novel detection opportunities for their analytical performance [31]. In addition, this method has been shown to be excellent tools in diagnostic applications. The portability and fast response are essential in many situations like illness diagnostics. One of the nanostructures is silica (SiO_2) nanoparticles functionalized by 3-mercaptopropyl trimethoxysilane (SN-MPTS) which was synthesized and characterized in the current study. Silica nanoparticles have good biocompatibility, large specific surface area and easy preparation [32]. In addition, it seems to existence sulfur atom in the structure of thiol modified nanoparticles lead to their bioactivity and its tendency to enzymes. Thiol as a potent nucleophile attacks on electron deficient center of protein in the nucleophilic reaction [33]. The application of these nanoparticles with Tyr leads to the co-catalytic effect and increase of sensitivity and decrease of the detection limit.

In this research, for the first time we presented a new biosensor for determination of L-tyrosine by using banana peel tissue Tyr (B.P.Tyr) enzyme immobilized on paper matrices which is modified with SN-MPTS on the surface of graphite screen printed electrode that is named B.P.Tyr/M/SN-MPTS/SPE. The paper based immobilization and the co-catalytic effect of Tyr and nanoparticles, lead to development an inexpensive, easy, fast, sensitive, miniaturized and portable device for L-tyrosine electrochemical determination.

2. Experimental

2.1. Reagents and solutions

All reagents were analytical grade. All solutions in this study were prepared in phosphate buffer solution (PBS, pH 7.0) containing double deionized distilled water, orthophosphoric acid and its disodium salt from Merck.

The Ecuador banana (*Musa cavendish*) was purchased at commercial maturity from a local store. Potassium hexacyanoferrate ($K_4Fe[CN]_6$) was obtained from Sigma-Aldrich. For synthesis of SiO_2-MPTS nanoparticles, ethanol from Merck, silica nanoparticles (SN) and mercapto propyl trimethoxy silica (MPTS) from Sigma-Aldrich were purchased. L-tyrosine and healthy human serum sample with ethical approval for real sample analysis were supplied by Fluka and Razi pathobiology lab., respectively. Their fresh solutions were prepared daily.

2.2. Instrumentation

Graphite screen printed electrodes (SPEs) and the boxed connector for SPEs were purchased from Florence, Italy. The working electrode was made of carbon (3 mm in diameter), counter and reference electrodes were made of carbon ring and silver chloride pseudo-reference electrode, respectively. Electrochemical studies were carried out using an Autolab PGstut 30 electrochemical analysis system controlled by GPES 4.9 and FRA software (Eco Chemie Netherlands). A Mira 3-XMU Field Emission scanning electron microscope was used for obtaining scanning electron microscopy images. FT-IR spectra were obtained on a Shimadzu instrument. Grade 1 filter paper (Whatman Asia Pacific PTE Ltd.) was cut with a paper punch for obtaining an immobilization area.

2.3. Preparation of SN-MPTS

To functionalities of silica nanoparticles (SN) with 3-mercaptopropyl trimethoxysilane (MPTS) groups, 0.1 g of SN was dispersed in 20 mL of ethanol. Then, 1 mL of MPTS was added to the mixture and stirred at 80°C for 6 h. The precipitate was filtered and the solid was washed with ethanol and dried at 40 °C to form SiO_2- MPTS (SN-MPTS).

2.4. Preparation of B.P.Tyr/M/SN-MPTS/SPE and its application to L-tyrosine determination

In preparation of immobilization area, Grade 1 filter paper was cut to round discs with 8 mm in diameter by a paper punch. The peel of mature washed Ecuador banana was grated and then the tissue was mixed with 0.1 M PBS (pH 7.0) to obtain 10% W/V mixture. The supernatant was kept as the source of enzyme and 5 µL of the banana peel extract was added to the paper discs. After being dried at room temperature (25ºC), 3 µL of 30 mM potassium hexacyanoferrate in 0.1M PBS as mediator was added to each paper disc and was put at room temperature to dry. Then, 5 µL of SN-MPTS solution in distilled water was dropped on each disc and allowed to dry at room temperature [34].

2.5. L-tyrosine electrochemical determination

Before each experiment, the paper disc as a source of Tyr was placed on the top of the SPE to cover all three electrodes system. Other discs were stored at 4 ºC for stability study. The modified SPE was connected to the potentiostat/galvanostat Autolab and applied for electrochemical determination of L-tyrosine amino acid. First, 3 µL of L-tyrosine solution with different concentrations was dropped on the paper. Then, 10 µL of 0.1 M PBS (pH 7.0) as supporting electrolyte was added onto the paper disc to have a suitable connection with SPE.

The DPV data on the surface of B.P.Tyr/M/SN-MPTS/SPE were obtained in a range between -0.5 to +0.8 vs. reference electrode at a scan rate of 50 mV s^{-1} with amplitude of 40 mV and a pulse width of 0.2 s. Furthermore, L-tyrosine concentrations in real samples were determined by a four-point standard addition method to evaluate the biosensor performance in com-

plex matrices. All measurements were replicated three times. The preparation method and electrochemical response of the mediated banana peel Tyr paper disc modified with SN-MPTS is shown in Scheme 1.

Here Scheme 1

3. Results and discussion

3.1. Characterization of SN-MPTS

To characterization the synthesized SN-MPTS, the analysis of FT-IR and FT-SEM was applied. Figure 1A shows the FT-IR spectra of the SN-MPTS. The peaks around 1010-1270 cm^{-1} are due to the Si–O–Si vibrations. The absorption bands at 1520-1680 cm^{-1} and 2535 cm^{-1} related to the C=O and S-H vibrations, respectively. These results show that MPTS groups were loaded into the SN. Also, the peaks at 2928 cm^{-1} and 3280-3530 cm^{-1}, attributed to the C–H stretching vibrations and O-H of silanols.

The morphology of synthesized nanoparticles was investigated by SEM images. Figs. 1B and C represent the FE-SEM images of the bare SPE and SN-MPTS modified SPE, respectively. Fig. 1C shows the spherical morphology of the immobilized SN-MPTS with sizes ranging from 21 to 32 nm on the surface of SPE. The nanoparticles have high efficiency that can be resulted in increasing amplification of the response signal because of their small size and high specific surface area. In addition the thiol modification, provide a tense binding between the nanoparticles and the Tyr to obtain an effective enzyme immobilization.

Here Fig. 1

3.2. Electrochemical characterization of biosensor

Cyclic voltammetry was applied to investigate of immobilization of Tyr and the effect of SN-MPTS on the response of biosensor. The cyclic voltammograms (CVs) of 50 µM of L-tyrosine at the surface of various electrodes such as bare SPE (curve a), M/SPE (curve b), B.P.Tyr/M/SPE (curve c) and B.P.Tyr/M/SN-MPTS/SPE (curve d) are shown in Fig. 2A. Curve b shows a couple of well-defined redox peaks related to $[Fe(CN)6]^{3-}$/$[Fe(CN)6]^{4-}$ redox couple. Curve c shows the catalytic effect of banana peel Tyr that was immobilized on the surface of the paper disc due to increasing the current value and negative shift of peak potential. After embedding of the SN-MPTS in the biosensor, the intensity of the redox signals increased (curve d) due to the larger electron transfer ability and specific surface area of nanoparticles as well as the higher biocatalytic effect of the enzyme that led to co-catalytic effect in this biosensor. This experiment was done without 50 µM of L-tyrosine by B.P.Tyr/M/SPE biosensor and curve b was obtained, that shows the catalytic effect of Tyr was missing without its substrate.

Furthermore, electrochemical impedance spectroscopy (EIS) as an effective and simple method for evaluating the electron transfer properties of the modified electrode was applied [35]. In this spectra, the diameter of the semicircle illustrates the interfacial electron transfer resistance (R_{et}) and the straight line shows the diffusion-limited process in electrochemical reactions [36]. ESI studies were carried out on each one of the electrodes in the presence of 1.0 mM $[Fe(CN)6]^{3-/4-}$redox couple and 0.1 M PB solutions (Fig.2B). The comparison of the obtained R_{et} values from curves (a) to (d) of Nyquist diagrams show increasing in electron transfer ability of redox probe. Therefore, the proposed biosensor has the least electrochemical impedance and the results of EIS analysis were in correspondence with the CV assays.

Here Fig. 2

3.3. Optimization experiment

The optimization of pH for the best activity and prevention of denaturation of the immobilized enzyme is necessary [37-39]. The impact of pH on the L-tyrosine electrochemical determination was studied at the surface of B.P.Tyr/M/SN-MPTS/SPE by DPV with the pH ranged from 4 to 10 in 0.1 M PBS. The paper based biosensor response to 100 µM of L-tyrosine was enhanced by increasing the pH from 4 to 7, while it was decreased in the pH ranged from 7 to 10 (Fig. 3A). The reduced response of the biosensor could be due to enzyme denaturation which resulted in missing of the biocatalytic activity [40]. So, the electrochemical determination of L-tyrosine has been done at optimum pH (pH 7.0) in all experiments.

The effect of the tissue percentage on the electrochemical response is important [41]. Different amount of banana peel tissue mixture in PBS, including 6%, 8%, 10% and 12% (W/V) were added to each paper with 30 mM of mediator solution and SN-MPTS. Then, the responses to100 µM of L-tyrosine for each disc were investigated by DPV. Increasing of the loaded tissue percentage was accompanied with increasing of the oxidation peak current of L-tyrosine (Fig. 3B). In the current study, we selected the level of tissue percentage at 10% (W/V). However, 12% (W/V) revealed the highest response; there was a probable interaction between tissue and sample matrices which caused to increasing in noise level.

The mediators have an important role in the function of biosensors to make a link between electroactive center of enzymes and the surface of the electrode [24]. As previously reported the effect of mediator loading on the response of biosensor has been studied [42]. In this study, different concentrations of hexacyanoferrate as a mediator solution in the range of 10-50 mM were loaded to different paper disc with 10% (W/V) tissue and SN-MPTS. The DPV responses of 200 µM of L-tyrosine (Fig. 3C) were enhanced by increasing mediator concentra-

tions. Although the signal was increased well in high level of mediator concentrations, we selected the medium level of mediator (30 mM) for subsequent experiments. This is due to increasing of the ratio of L-tyrosine electrocatalytic oxidation current to mediator oxidation current.

Here Fig. 3

3.4. L-tyrosine biosensor response characteristics

The electrochemical determination of L-tyrosine was done at optimum condition (10% (W/V) tissue mixture, 30 mM of hexacyanoferrate and PBS at pH 7.0) by using of DPV method. The oxidation peak of L-tyrosine was increased by increasing of L-tyrosine concentration (Fig. 4A). The linear response range of the biosensor between 0.05 and 600 µM of L-tyrosine is shown in Fig. 4B. One of the advantages of this biosensor is a wide linear range with a linear regression equation of $y=0.460x+46.30$ and high linearity ($R^2=0.994$). In this equation y agent is the current in µA and x indicates the L-tyrosine concentration in µM. Based on the standard deviation of the blank signal (n=10), the limit of detection (LOD) and limit of quantity (LOQ) were 0.02 µM and 0.06 µM, respectively. The relative standard deviation of this method at 10 µM of L-tyrosine was 3.5% which is describing a good repeatability. To estimate the reproducibility of B.P.Tyr/M/SN-MPTS/SPE, eight paper based biosensor were prepared for the determination of 10 µM of L-tyrosine. The result showed that relative standard deviation between eight experiments was 3.8%, indicated good reproducibility. To investigate the biosensor stability, sixteen B.P.Tyr/M/SN-MPTS paper was prepared and kept at 4 ˚C. The responses of these biosensors to 150 µM of L-tyrosine were evaluated every five days up to 2 months. The results showed the biosensor response retained almost 80% of the initial value after 2 months (Fig. S1). It seems that the biosensor represents good stability. The comparison of the B.P.Tyr/M/SN-MPTS/SPE char-

acterizations with another type of L-tyrosine biosensors (table 1) indicates the linear range of proposed biosensor was notably wider than the other biosensors and the LOD is lower than the others. In this study, we presented a simple, low cost and speed method to voltammetric determination of L-tyrosine.

Here Fig. 4

Here Fig. S1

Here Table 1

3.5. Selectivity study

For investigation of interferences impact, the application of B.P.Tyr/M/SN-MPTS/SPE biosensor was studied at 200 µM of L-tyrosine in the presence of different biomolecules. The biomolecules such as L-phenylalanine, L-tryptophan, L-serine, glucose, fructose, urea and uric acid, similar to concentration of L-tyrosine, were used in the current study. The oxidation peak currents of the biosensor to the interferences were lower than the peak current of L-tyrosine (Fig.S2). This result demonstrates excellent selectivity of this biosensor to L-tyrosine due to the specific interaction between the enzyme and substrate.

Here Fig. S2

3.6. Practical application on real samples

In order to get the applicability of B.P.Tyr/M/SN-MPTS/SPE biosensor, determination of L-tyrosine was done in heparinized human blood plasma matrices after pretreatment [43]. Healthy human plasma sample was supplied by the Razi pathobiology laboratory (Babol, Iran) with ethical approval. Recovery performance was carried out by the spiking of different quanti-

ties of the standard L-tyrosine solutions. Three independent assays (n=3) for each measurement were applied (table 2). The results are in accordance with the calibration curve. The initial amount of L-tyrosine in plasma was determined by the HPLC method (in the Razi pathobiology lab.) and this method at 61.57 and 60.34 µM, respectively (n=3). The t and F- tests were carried out [44]. F_{cal} that calculated F value was 9.25 and T_{cal} that calculated t value was 3.92. The critical values of F and t (for 95% probability) are 19 and 4.30, respectively. The comparison of these data indicates that there is no systematic error between these two methods. Therefore, there is a satisfactory performance of this method for voltammetric determination of the total L-tyrosine concentration in real samples.

Here Table 2

4. Conclusion

In this study a powerful enzymatic biosensor for L-tyrosine determination in standard solutions and real samples was developed. A real source of Tyr (banana peel) was applied on a paper disc with SN-MPTS in the presence of hexacyanoferrate. The effects of the specific catalytic activity of Tyr and sensitivity enhancing properties of SN-MPTS lead to the wide linear concentration range, low LOD and fast response time of the biosensor. However, the amount of enzyme in each tissue is different and the results may have a little deviation in each experiment by changing in the tissue, which the deviation can be resolved by calibration method. This biosensor was easily prepared and showed outstanding selectivity and stability. Furthermore, the use of paper based biosensor and SPE leads to miniaturization and portable ability of this technique. The low cost, simple and fast fabrication method of the biosensor are its advantages to other methods.

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Appendix A. Supplementary data

The following are Supplementary data:

Stability and selectivity results of the biosensor

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Figures legends:

Scheme 1. The procedure of fabrication of the B.P.Tyr/M/SN-MPTS biosensor for electrochemical determination of L-tyrosine

Fig. 1. (A) FT-IR spectra of synthesized SN-MPTS, (B) and (C) FE-SEM images of bare SPE and SN-MPTS modified SPE, respectively

Fig. 2. Characterization of different modification steps by (A) CVs in 50 µM of L-tyrosine and (B) EIS in 1.0 mM $[Fe(CN)_6]^{3-/4-}$ redox couple and 0.1 M PB solutions, obtained at the surface of (a) bare SPE, (b) M/SPE, (c) B.P.Tyr/M/SPE and (d) B.P.Tyr/M/SN-MPTS/SPE in 0.1 M phosphate buffer solution (pH 7.0)

Fig. 3. Optimization of the experimental parameters: effect of (A) pH, (B) banana peel tissue percentage, (C) mediator loading concentration on the B.P.Tyr/M/SN-MPTS/SPE response

Fig. 4. DPV signals of various concentrations of L-tyrosine (a) 0.05, (b) 20, (c) 50, (d) 85, (e) 100, (f) 130, (g) 150, (h) 200, (i) 300, (j) 400, (k) 500 µM and (l) 600 µM in 0.1 M phosphate buffer solution (pH 7.0) at a scan rate of 50 mVs^{-1} with an amplitude of 40 mV and pulse width of 0.2 s. Inset: Calibration curve of the electrochemical response (I_{peak}) vs. L-tyrosine concentration.

Table 1.

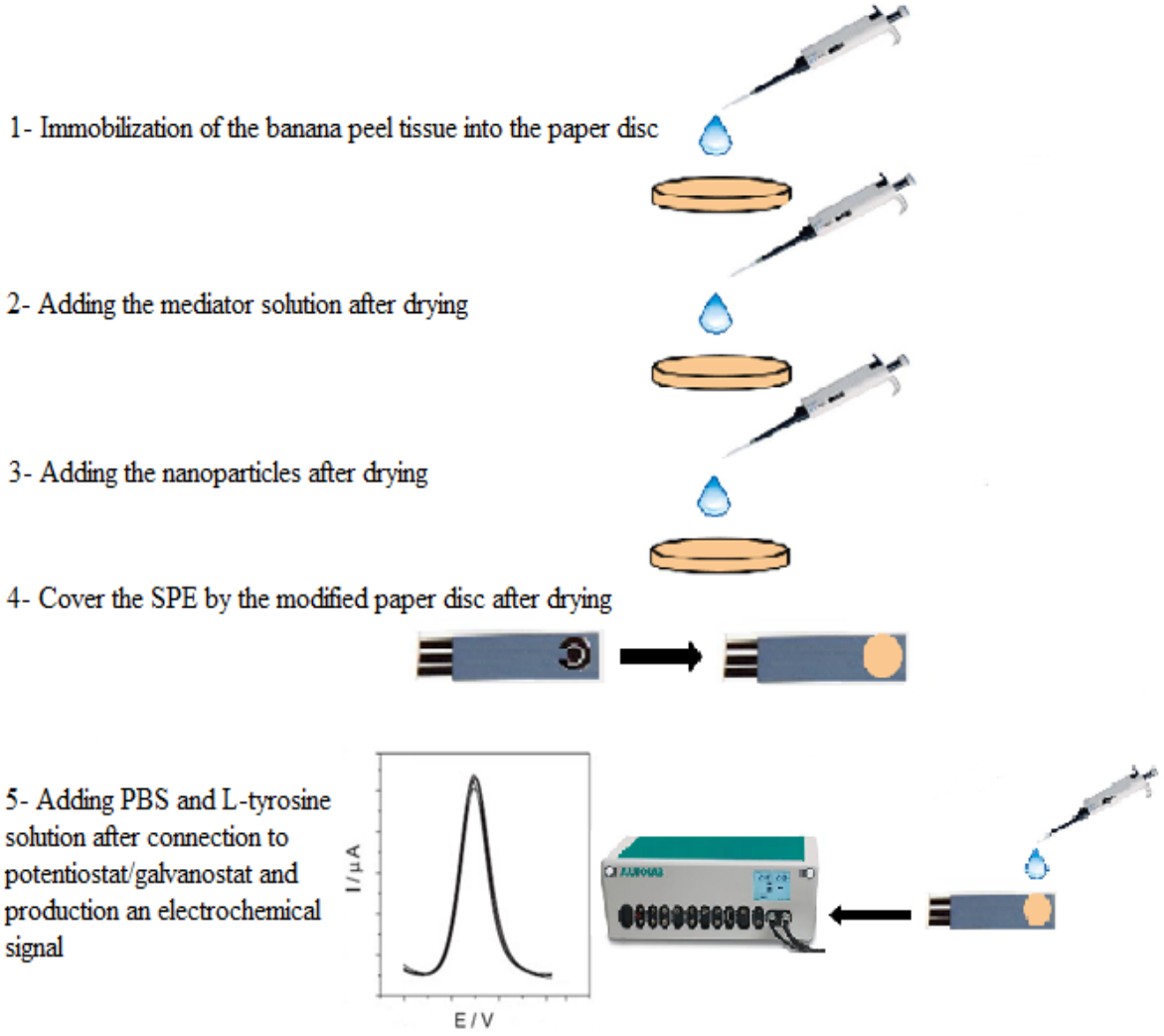
Analytical performance characteristics of some L-tyrosine biosensors

Electrode	Detection Limit (µM)	Linear Range (µM)	Ref.
BuCh, GCE	0.4	4 - 100	[1]
MWCNT, ionic liquid, copper(II), GCE	0.008	0.01 - 5	[45]
Boron-doped diamondelectrode	1	100 - 700	[46]
MWCNT/4-amino benzene sulfonic acid, GCE	0.08	0.1 - 50	[47]
L-serine polymer film electrode	0.1	0.3 - 100	[48]
Tyrosinase/PANI-PVS/BDD electrode	0.01	2 - 6	[49]
Zeolite, carbon paste electrode	0.32	1.26 - 90	[50]
Gold nanoparticles, GCE	0.04	0.1 - 300	[51]
B.P.Tyr/M/SN-MPTS/SPE	0.03	0.05 - 600	This work

Table 2.

Analysis of heparinized blood plasma sample with different concentrations of L-tyrosine

Sample	$C_{L\text{-tyrosine}}$/added (µM)	$C_{L\text{-tyrosine}}$/detected (µM)	Recovery (%)	RSD (%)
1	10.0	9.4	94.0	2.5
2	150.0	151.9	101.2	1.2
3	350.0	353.4	101.0	1.8
4	400.0	405.8	101.4	2.7



Scheme 1

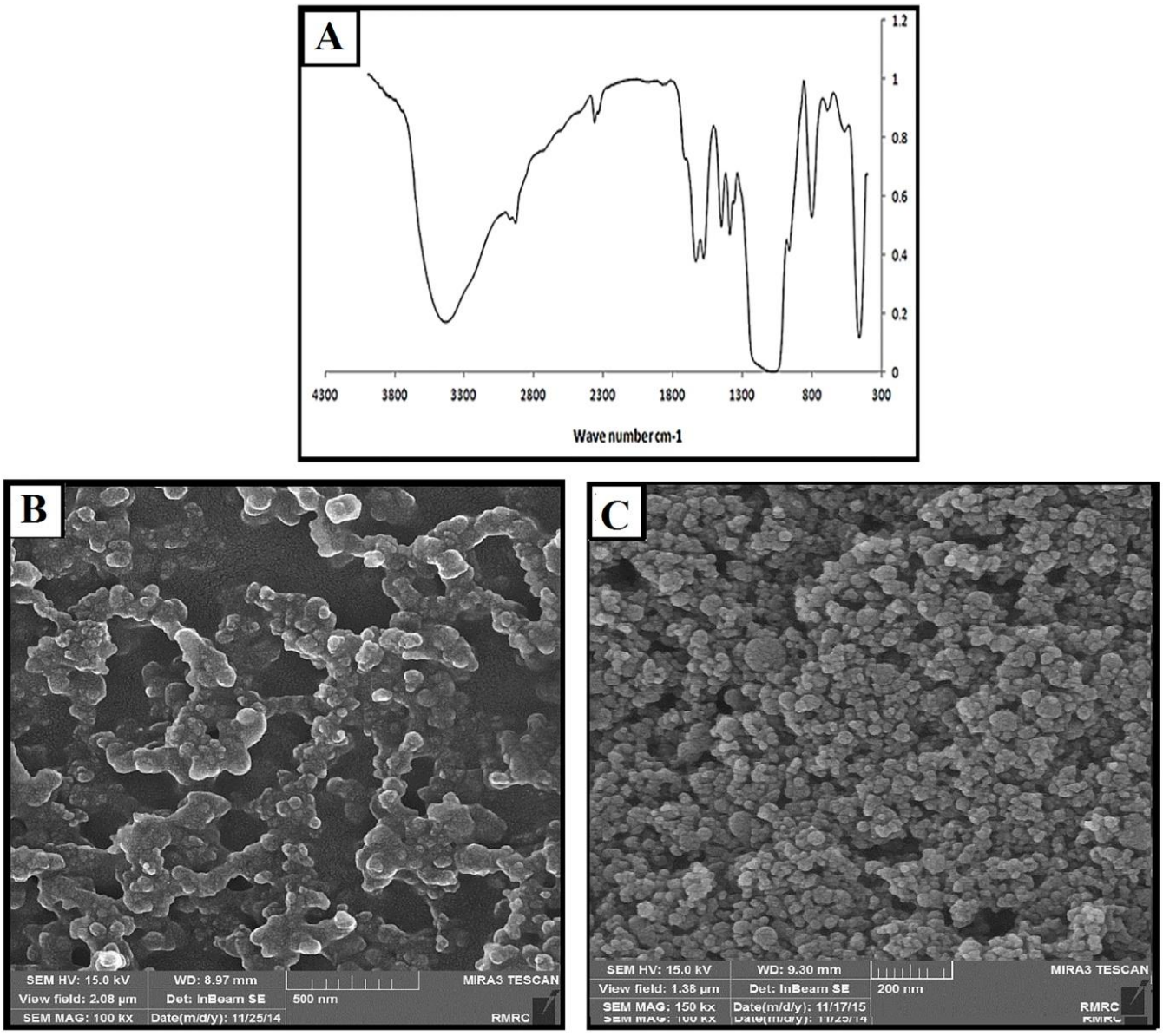


Fig. 1

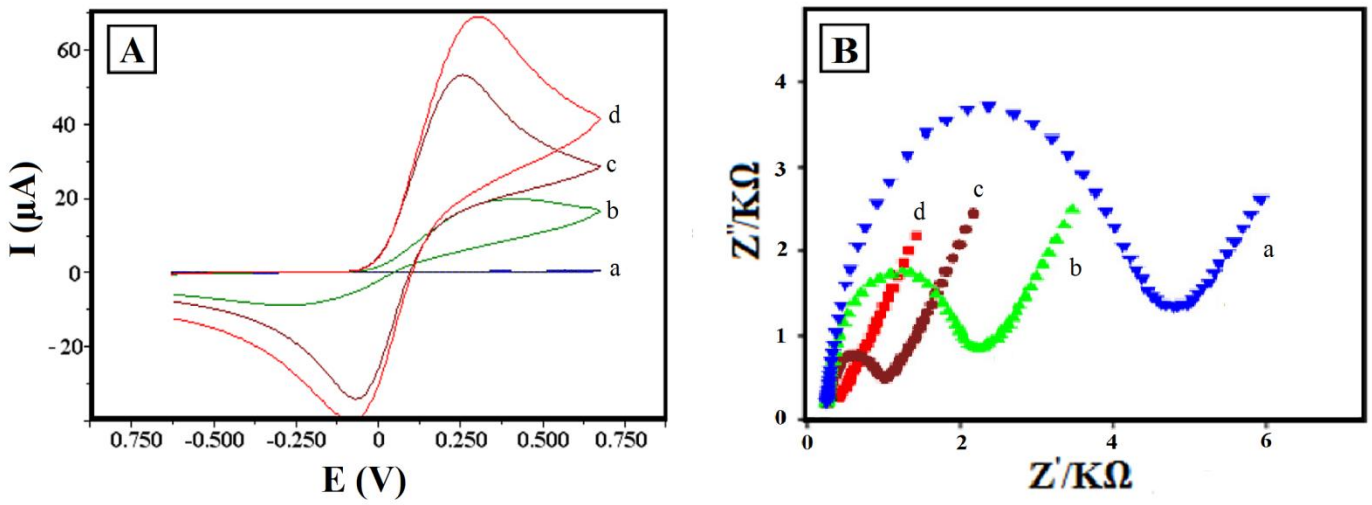


Fig. 2

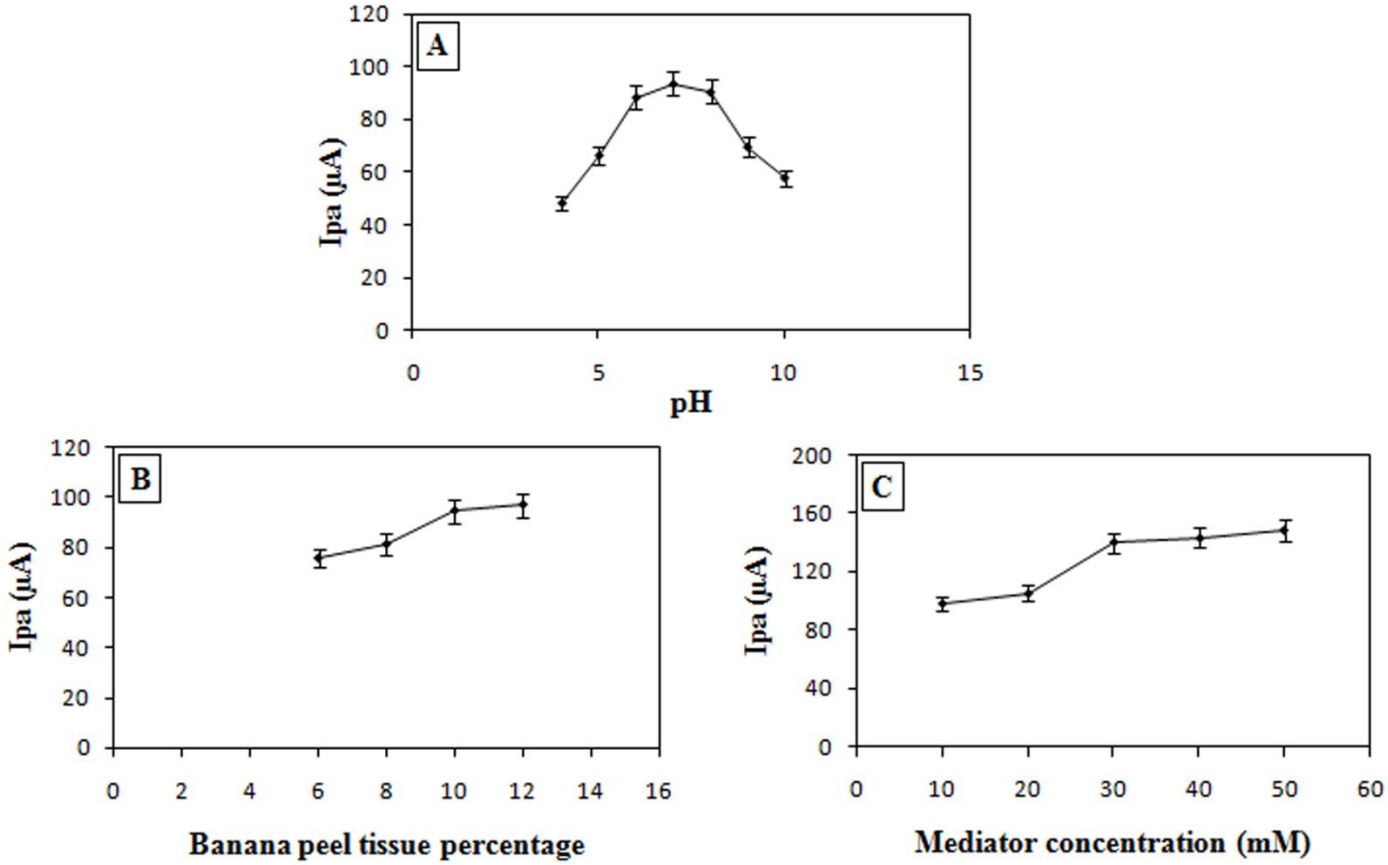


Fig. 3

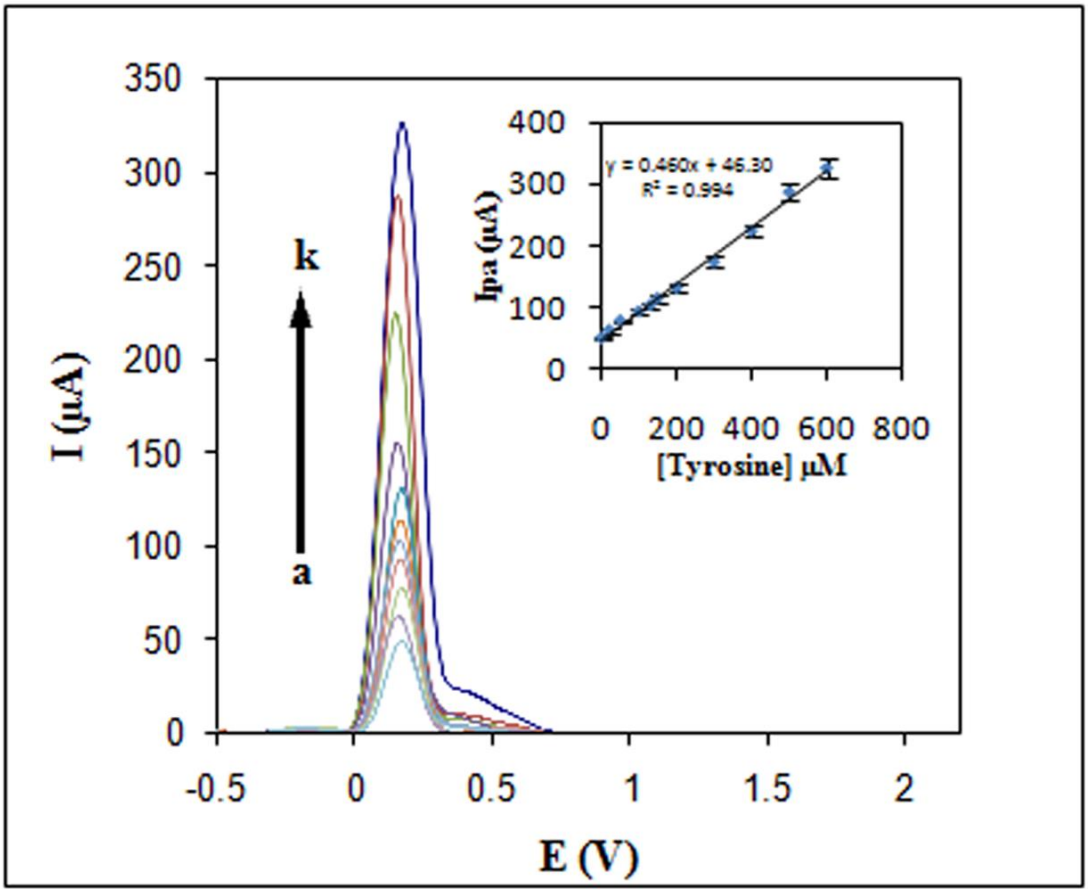


Fig. 4

Supplementary Information

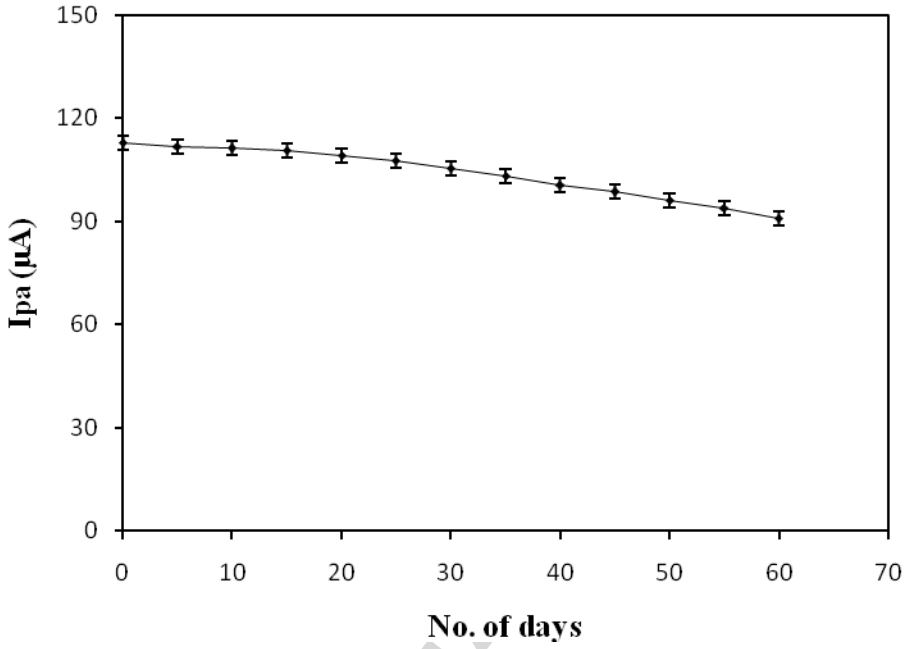


Fig. S1. The Banana Peel Tyr/M/SN-MPTS/SPE stability in the DPV determination of 10 µM of L-tyrosine in 0.1 M phosphate buffer solution (pH 7.0)

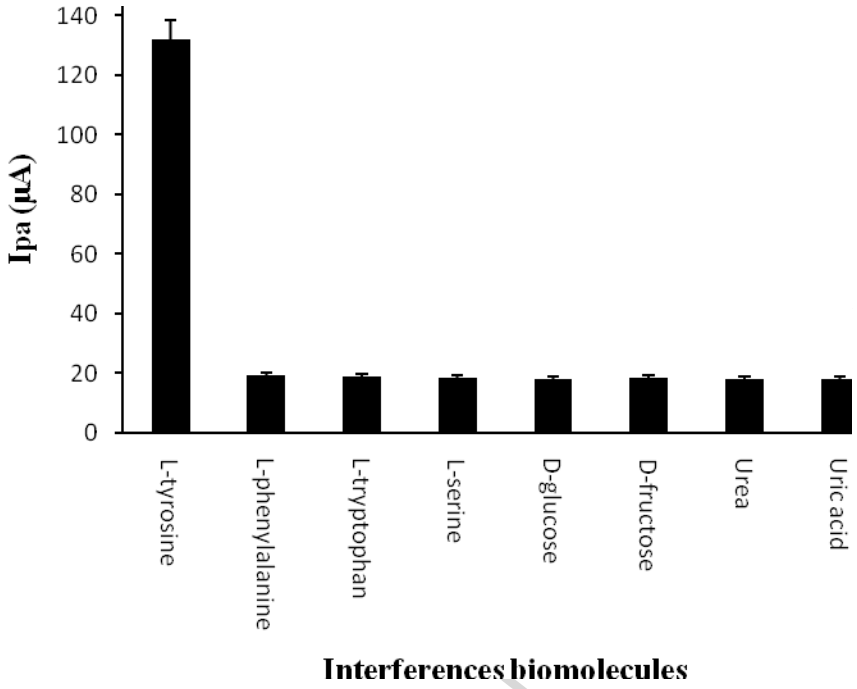


Fig. S2. The selectivity test of the prepared biosensor for voltammetric determination of L-tyrosine in the presence of some interference biomolecules in 0.1 M phosphate buffer solution (pH 7.0)