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Rapid and Sensitive Electrochemical Monitoring of Tyrosine Using NiO Nanoparticles Modified Graphite Screen Printed Electrode

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NiO nanoparticles was employed for the sensitive determination of tyrosine. The electrochemical response characteristics of the modified electrode toward the tyrosine was investigated by cyclic voltammetry (CV), chronoamperometry (CHA) and differential pulse voltammetry (DPV). The response of the electrochemical sensor for the tyrosine was found to be improved significantly in comparison with those obtained at graphite screen printed electrode (SPE). The oxidation peak current increased linearly in the range of 0.15-450.0 µM, with the detection limits of 0.1 µM.

Keywords: Tyrosine, NiO nanoparticles, Voltammetric sensor, Graphite screen printed electrode

1. INTRODUCTION

Tyrosine (Tyr) is one of the amino acids which is necessary for the maintenance of nutritional balance. The content of tyrosine in the body is correlated to the healthy state of the person [1,2]. Tyrosine is a precursor for thyroxin, dopa, dopamine, noradrenalin and adrenalin as the hormone or non-tuberculosis mycobacterial in central nervous systems [3]. Some diseases such as hypochondrium, depression and other psychological diseases can be observed in the absence of tyrosine [4,5]. Many analytical methods have been reported for the determination of tyrosine [6-10]. However, most of them are limited by some disadvantages. Electrochemical methods provide a simple, low-cost and fast way for analysing biologically and environmentally important substances [11-21].

A screen-printed electrode (SPE) is an attractive alternative choice due to their miniaturized size, inexpensive, easy to fabricate, rapid responses and disposable, which makes them especially

suitable for on-site analysis [22-26]. Unfortunately, amino acids have a poor electrochemical response at solid electrodes therefore, chemical modifications are employed to improve their electrochemical response [27-32]. Nanosized materials have high surface area-to-volume ratio, provide a decrease of the overpotential of many analytes that occur at unmodified electrodes, increase the magnitude of the voltammetric response, and result in faster electron transfer between the electrode and analyte [33-45].

In the past decades, the investigations on the direct electrochemistry and electrochemical applications of nanoparticles have aroused considerable interest in analytical chemistry and bioinorganic chemistry [46-51]. Among transition metal oxides, nickel oxide (NiO) nanoparticles has attracted enormous interest due to its wide range of applications in various fields and outstanding properties such as large specific capacitance for supercapacitor electrodes, lithium ion batteries, wide bandgap (~3.88 eV), stable endurance for resistive switching, high carrier density, rapid switching time for resistance-based memory, dye-sensitized solar cells, and electrochromic devices [52-55].

Therefore, in this work, the preparation and electrochemical characterization of NiO nanoparticles modified screen printed electrode (NiO/SPE), as well as, its behavior as electrocatalyst toward the oxidation and sensitive determination of tyrosine were investigated.

2. EXPERIMENTAL

2.1. Chemicals and Apparatus

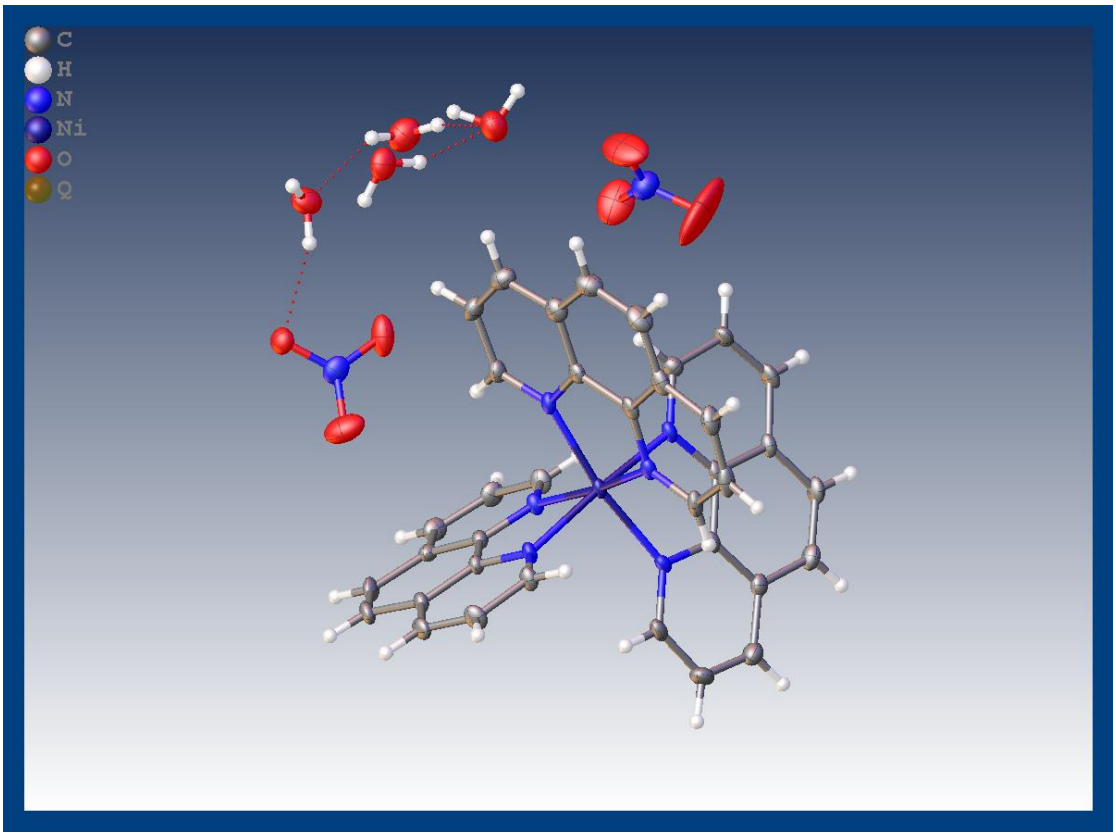
An Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands) was employed to perform the electrochemical experiments and the system was controlled using a general purpose electrochemical system software. The crystal structure of $[Ni(Phen)_3](NO_3)_2.4H_2O$ was obtained via the single-crystal X-ray diffraction technique.

The screen-printed electrode (DropSens, DRP-110, Spain) consists of three conventional electrodes: graphite counter electrode, a silver pseudo-reference electrode and an unmodified graphite working electrode. pH was measured by a Metrohm 710 pH meter.

Tyrosine and all other reagents were analytical grade, and were purchased from Merck (Darmstadt, Germany). For the preparation of buffers, the orthophosphoric acid and its salts were used to provide the pH range of 2.0–9.0.

2.2. Preparation of $[Ni(Phen)_3](NO_3)_2.4H_2O$ complex

1,10-phenanthroline (3 mmol) was dissolved in 15 ml distilled water containing NaOH (6 mmol) and stirred 30 min, at room temperature. An aqueous solution of $Ni(NO_3)_2.6H_2O$ (1.0 mmol) was added to the above-mentioned solution. The reaction mixture was placed in a Parr-Teflon lined stainless steel vessel. It was sealed and heated to 120 °C for 8 h. The reaction mixture was cooled by slow cooling to the room temperature. Pink crystals of $[Ni(Phen)_3](NO_3)_2.4H_2O$ (Scheme 1) suitable for single crystal X-ray diffraction analysis were collected from the final reaction mixture by filtration and air dried at the ambient temperature.



Scheme 1. Crystal structure of $[Ni(Phen)_3](NO_3)_2.4H_2O$

2.3. Synthesis of NiO nanoparticles

The NiO nanoparticles was obtained through calcinations of $[Ni(Phen)_3](NO_3)_2.4H_2O$ precursor at 700 °C at the atmosphere of static air in the electric furnace and maintaining in this temperature for 6 h.

2.4. Preparation of the electrode

The bare graphite screen printed electrode was coated with NiO nanoparticles (NiO/SPE) according to the following simple procedure. 1 mg NiO nanoparticles was dispersed in 1 mL aqueous solution within 45 min ultrasonication. Then, 5 µl of the prepared suspension was dropped on the surface of carbon working electrodes. It remains at room temperature until becomes dry.

2.5. Preparation of real samples

10 mL of each urine sample was taken from the original sample stored in a refrigerator and at 2000 rpm for 15 minutes, and then the supernatant was filtered with a 0.45 µm filter. Then known volumes of the solution were taken and diluted in a 25 mL flask using PBS (pH=7.0). Eventually the samples were spiked with known quantities of tyrosine.

3. RESULT AND DISCUSSION

3.1. Electrochemical profile of the tyrosine on the NiO/SPE

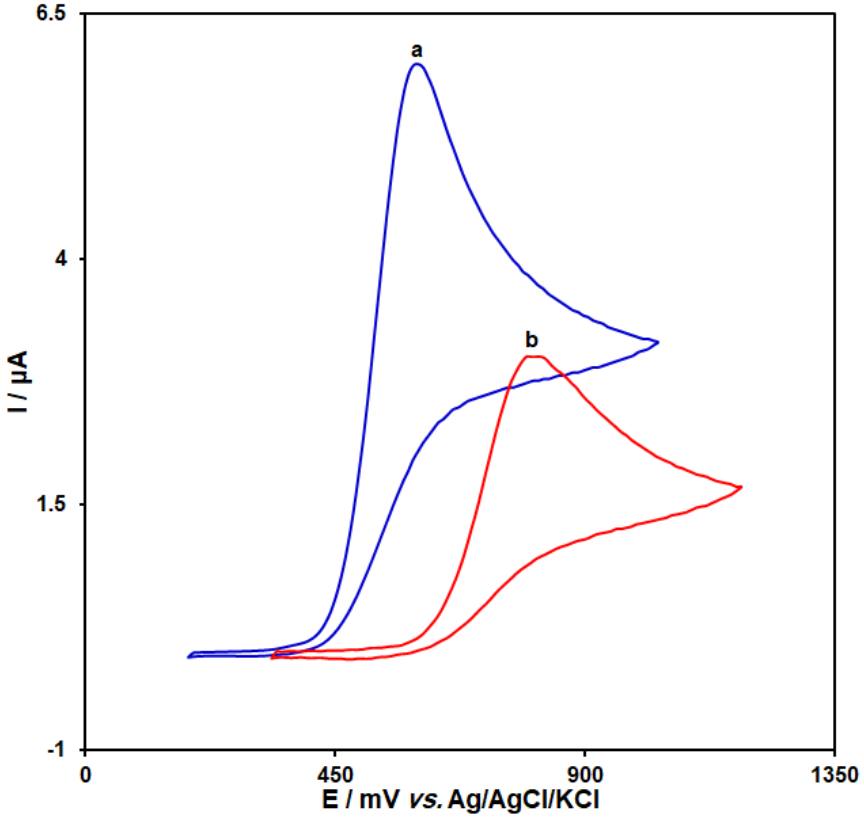


Figure 1. Cyclic voltammograms of (a) NiO/SPE and (b) bare SPE in 0.1 M PBS (pH 7.0) in the presence of 250.0 µM tyrosine at the scan rate 50 mVs^{-1}.

The obtained cyclic voltammograms in the presence of 250.0 µM tyrosine using NiO/SPE the (Curve a) and bare SPE (Curve b) are shown in Fig. 1. According to CV results the maximum oxidation of tyrosine on the NiO/SPE occurs at 600 mV which is about 210 mV more negative compared with unmodified SPE.

3.2. Effect of scan rate on the results

Increasing in scan rate leads to enhanced oxidation peak current according to the obtained results from the study of the effect of potential scan rates on the oxidation currents of tyrosine, Fig. 2.

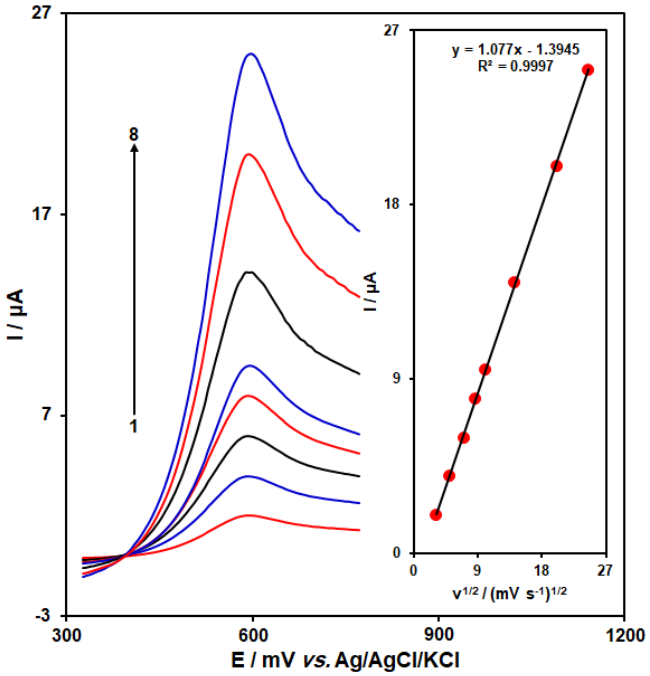


Figure 2. Linear sweep voltammograms (LSVs) of NiO/SPE in 0.1 M PBS (pH 7.0) containing 250.0 µM tyrosine at various scan rates; numbers 1-8 correspond to 10, 25, 50, 75, 100, 200, 400, and 600 mV s^{-1}, respectively. Inset: variation of anodic peak current vs. $\nu^{1/2}$.

In addition, there is a linear relationship between Ip and the square root of the potential scan rate ($\nu^{1/2}$) that demonstrates that the oxidation procedure of analyst is in control of diffusion.

3.3. Chronoamperometric analysis

Different tyrosine solutions in PBS (pH=7.0) were also used in chronoamperometric tests using NiO/SPE at 650 mV and the results are illustrated in Fig.3. It is known that for electroactive materials the electrochemical currents observed under mass-transport-limited conditions follow Cottrell's equation [56]. Best fit I vs. $t^{-1/2}$ curves plotted based on experimental data obtained for different tyrosine solutions are illustrated in Fig. 3A, and the slopes of these lines were next plotted vs. tyrosine concentration and the results are given in Fig. 3B. Using the slopes and Cottrell's equation the mean value for the diffusion coefficient (D) of the analyte was determined to be 4.2×10^{-6} cm^2/s.

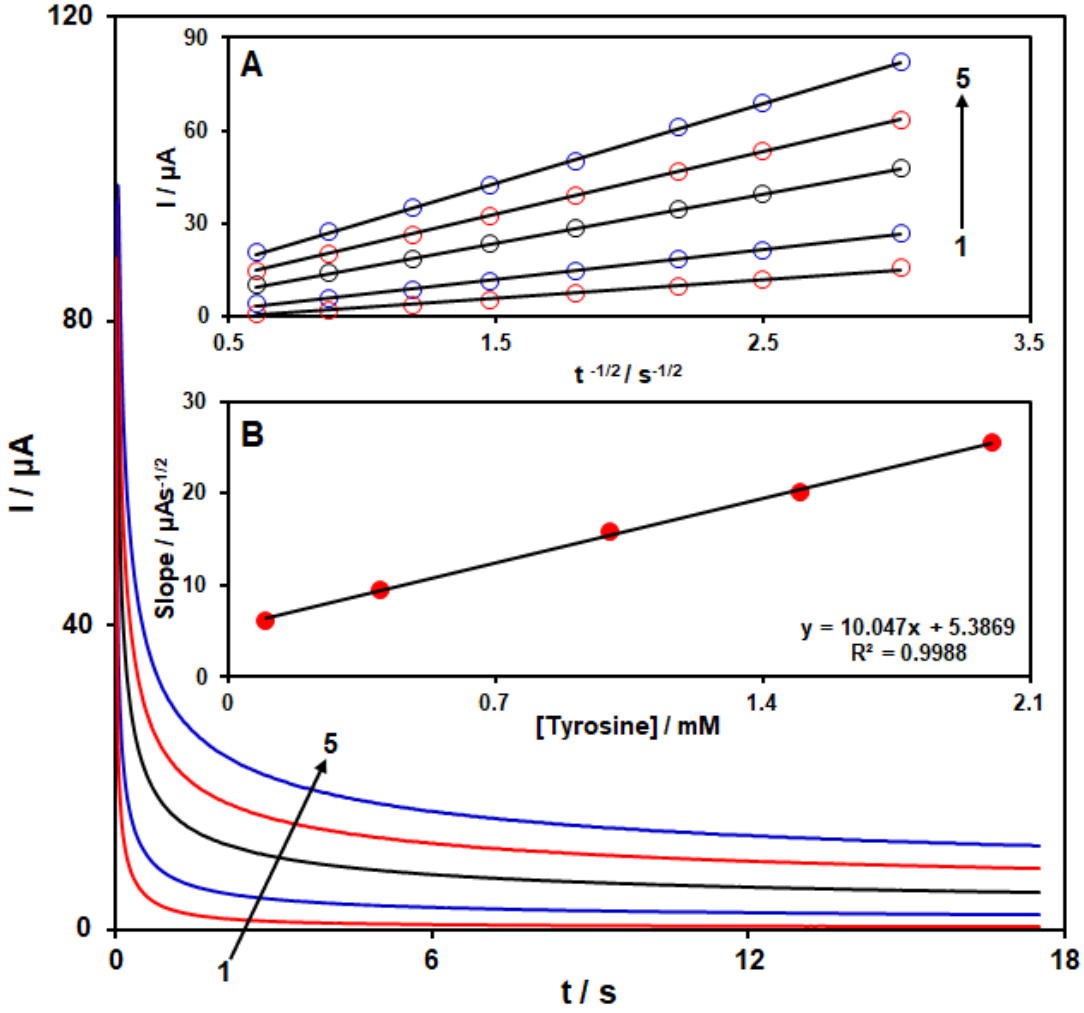


Figure 3. Chronoamperograms obtained at NiO/SPE in 0.1 M PBS (pH 7.0) for different concentration of tyrosine. The numbers 1–5 correspond to 0.1, 0.4, 1.0, 1.5 and 2.0 mM of tyrosine. Insets: (A) Plots of I vs. $t^{-1/2}$ obtained from chronoam chronoamperograms 1–5. (B) Plot of the slope of the straight lines against tyrosine concentration.

3.4. Calibration curves

The results of DPVs studies on different tyrosine solutions are illustrated in Fig. 4 as a plot of peak current vs. tyrosine concentration. The curve was found to be linear over concentration window ranging from 0.15 to 450.0 µM. The limit of detection (3σ) was also determined to be 0.1 µM. The detection limit was obtained 0.1 µM. The results are compared with previous works in table 1.

3.5. Analysis of real samples

The electrode was also used to determine tyrosine in urine, and the observations are given in table 2, where the reproducibility has been expressed in terms of the mean relative standard deviation (R.S.D.). The results are indicative of satisfactory recoveries for all of the tested species.

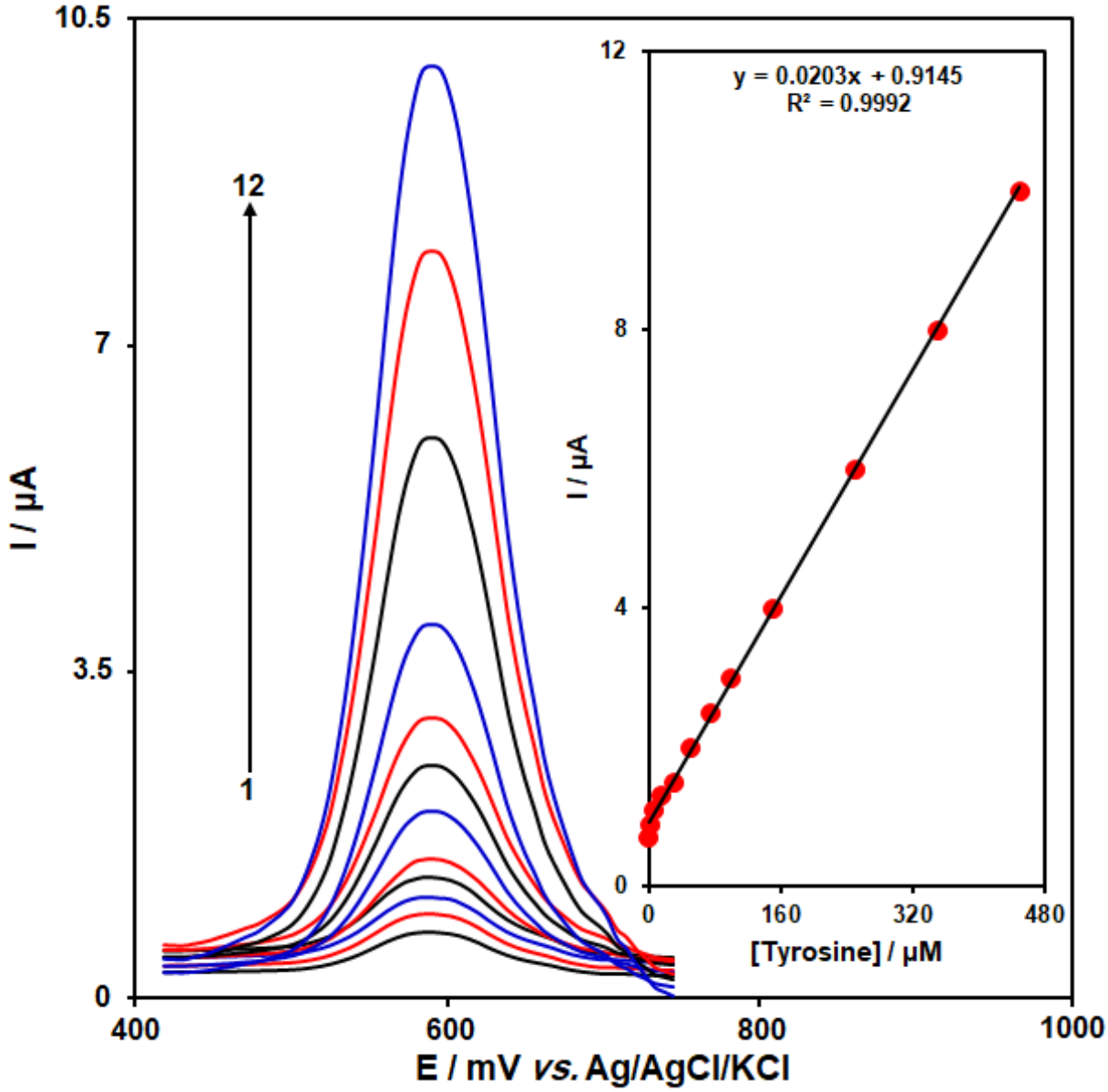


Figure 4. DPVs of NiO/SPE in 0.1 M (pH 7.0) containing different concentrations of tyrosine. Numbers 1–12 correspond to 0.15, 3.0, 7.0, 15.0, 30.0, 50.0, 75.0, 100.0, 150.0, 250.0, 350.0 and 450.0 µM of tyrosine. Inset: plot of the electrocatalytic peak current as a function of tyrosine concentration in the range of 0.15-450.0 µM.

4. CONCLUSIONS

In summary, NiO nanoparticles were synthesized. Finally, a screen printed electrode was fabricated using NiO nanoparticles to provide a sensitive electrochemical devise in tyrosine sensing. The detection limit of the method for tyrosine was 0.1 µM (*S/N* = 3) and the response was found to be linear in the concentration range of 0.15 to 450.0 µM. The modified electrode was use for the detection of tyrosine in real samples and found to produce satisfactory results.

Table 1. Comparison of the efficiency of electrochemical methods used in detection of tyrosine.

Method	Modifier	LOD	LDR	Ref.
Voltammetry	Palladium-platinum bimetallic alloy nanoparticles/chitosan-1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide/graphene-multiwalled carbon nanotubes-IL	0.009 nM	0.01-160.0 nM	[57]
Voltammetry	Mesoporous silica nanoparticles	0.034 μM	0.05-400.0 μM	[58]
Voltammetry	$ZnFe_2O_4$ nanoparticles	0.1 μM	0.4-175.0 μM	[59]
Voltammetry	Silica nanoparticles	0.0497 μM	0.3-600.0 μM	[60]
Voltammetry	Poly(threonine)	0.01 μM	0.5-200.0 μM	[61]
Voltammetry	Au nanoparticles/poly(E)-4-(p-tolyldiazenyl)benzene-1,2,3-triol	2.0 μM	10.0-560.0 μM	[62]
Voltammetry	NiO nanoparticles	0.1 μM	0.15-450.0 μM	This work

Table 2. The application of NiO/SPE for determination of tyrosine in tyrosine tablet and urine samples (n=5). All concentrations are in μM.

Spiked	Found	Recovery (%)	R.S.D. (%)
0	-	-	-
7.5	7.4	98.7	2.8
12.5	12.7	101.6	1.9
17.5	17.8	101.7	2.4
22.5	21.9	97.3	3.1

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