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Full Paper

rGO/ZnO Nanocomposite Modified Carbon Paste Electrode as Sensor for Tyrosine Analysis

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Abstract- Tyrosine is an important amino acid with wide application in human body. So, we try for fabrication of a fast electrochemical tyrosine sensor based on carbon paste electrode modified with reduced graphene oxide/ZnO nanocomposite (rGO/ZnO-NC/CPE). In the first step, we synthesized rGO/ZnO by chemical precipitation method and characterized by SEM and EDAX methods. The rGO/ZnO-NC/CPE showed highly catalytic activity to tyrosine electro-oxidation in aqueous solution. The anodic peak current of tyrosine increased with concentration of this amino acid in the ranges of 0.1–400 µM with limit of detection ~0.07 µM. The performance of rGO/ZnO-NC/CPE was check for the analysis of tyrosine in water and pharmaceutical serum samples.

Keywords- Tyrosine, Reduced graphene oxide/ZnO nanocomposite, Voltanetry, Senso

1. INTRODUCTION

Amino acids are a main group of biological materials that are necessary for body activity [1]. Amino acids can be derived in two important categories included essential and non-essential amino acids. Essential amino acid cannot make by the human body. The level of amino acids in human body is very important and it is a sign for human healthy. Therefore, doctors check amino acid level for study healthy of humans.

Tyrosine is a non-essential amino acid that makes by the human body and can be used for building proteins. Tyrosine builds by phenylalanine (phenyl alanine as an essential amino acid) in human body. Improve age-related wrinkles can be obtained using tyrosine at a surface of skin.

Therefore electrochemical sensors were suggested for analysis of tyrosine in biological or other pharmaceutical samples [2-4]. Due to fast response and good selectivity of electrochemical sensors many published paper tried for suggestion of new electrochemical sensors for biologica, drug or environmental samples analysis [5-15].

Carbon based nanomaterials and especially graphene nano-sheet showed different properties compare to graphite powder such as good electrical conductivity [16]. Good electrical conductivity can be useful for fabrication of highly sensitive sensors in electro-active compound analysis [17-19].

Therefore, in the presence study and due to important of tyrosine analysis in biological samples, we fabricated a highly sensitive and good selective electro-analytical sensor for tyrosine analysis. The presence sensor was fabricated by modification of carbon paste electrode with rGO/ZnO-NC. The rGO/ZnO-NC/CPE showed good ability for analysis of tyrosine in water and pharmaceutical serum samples. The fast response, good selectivity and highly sensitivity are main advantage of rGO/ZnO-NC/CPE as a tyrosine sensor.

2. EXPERIMENTAL

2.1. Materials and instruments

We use an Autolab, potentiostat/galvanostat for all of the voltammetric study. The rGO/ZnO-NC/CPE, Ag/AgCl/KCl and pt wire were used a working, reference and counter electrodes. A KYKY-EM3200 digital scanning electron microscope was used for morphological investigation. All of the chemicals reagent such as tyrosine, phosphoric acid, Zinc nitrate were of A.R. grade and were used as unless otherwise stated from Sigma-Aldrich.

2.2. Preparation of rGO/ZnO-NC/CPE

rGO/ZnO-NC/CPE was prepared by mixing of 0.1 g of rGO/ZnO-NC and graphite powder in the presence suitable amount of graphite powder. Then previous sample was mixed well for 50 min until a uniformly wetted paste was obtained. A portion of the paste was filled firmly into one glass tube as described above to prepare rGO/ZnO-NC/CPE.

2.3. Preparation of real samples

The water and pharmaceutical serum samples were used for analysis of tyrosine in real sample without any pretreatment procedure.

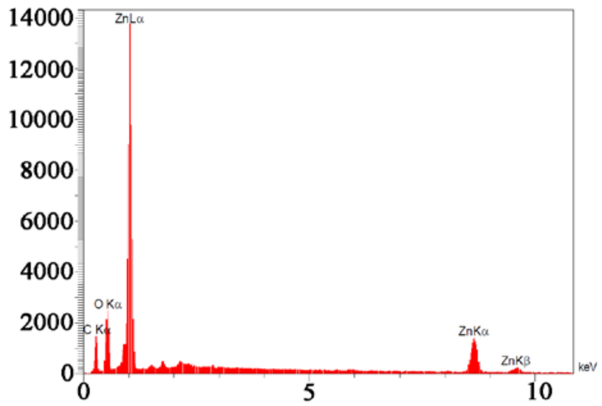
2.4. Synthesis procedure of rGO/NiO-NC

The 1.0 g graphene nanosheet disperses in 50 mL sodium hydroxide (1.0 M). The 50.0 mL zinc nitrate 0.5 M was added to sodium hydroxide solution. The dark sediment filtered and dry at 100 ^{o}C for 12 h ad then calcined at 250 ^{o}C for 2.0 h.

3. RESULTS AND DISCUSSION

3.1. rGO/ZnO-NC characterization

In the first step and before fabrication of modified electrode we characterized rGO/ZnO-NC by EDAX analysis and analysis data are presence in Figure 1.



Quantitative Results

Elt	Line	Int	Error	K	Kr	W%	A%	ZAF	Pk/Bg	LConf	HConf
C	Ka	163.0	32.2226	0.1352	0.0713	31.82	56.80	0.2241	60.24	30.91	32.72
O	Ka	296.5	30.9994	0.1225	0.0646	20.58	27.59	0.3139	71.76	20.15	21.02
Zn	Ka	378.6	2.5663	0.7423	0.3916	47.60	15.61	0.8226	31.67	46.71	48.49
				1.0000	0.5275	100.00	100.00				

Fig. 1. EDAX analysis data for rGO/ZnO-NC synthesized in this work

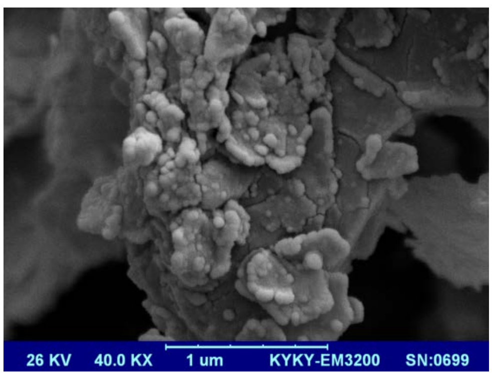


Fig. 2. SEM image of rGO/ZnO-NC synthesized in this work

According to the Figure 1 data, the presence of C, O and Zn elements confirms rGO/ZnO. The morphology of rGO/ZnO is presence in Figure 2 that showed spherical shape ZnO nanoparticle at a surface of r-GO nanosheet (Figure 2).

3.2. Electrochemical investigation

The catalytic activity of rGO/ZnO-NC/CPE was investigated by square wave voltammetric investigation of 180 μM tyrosine at pH=7.4 as biological condition. Figure 3 curve a and curve b showed square wave voltammograms of 180 μM tyrosine at a surface of rGO/ZnO-NC/CPE.

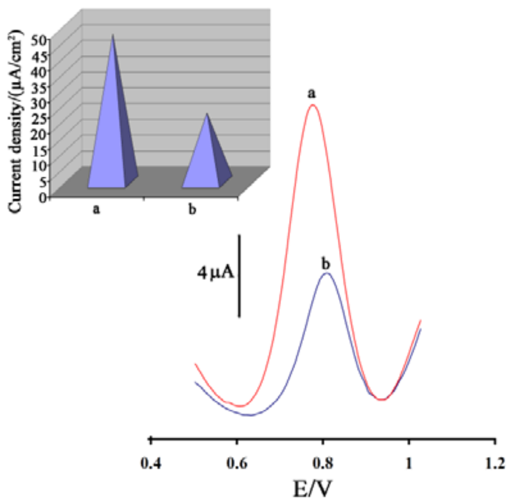


Fig. 3. Square wave voltammograms of (a) rGO/ZnO-NC/CPE and (b) CPE in the buffer solution pH=7.4 in the presence of 180 μM tyrosine. Inset: the current density derived from square wave voltammogram responses

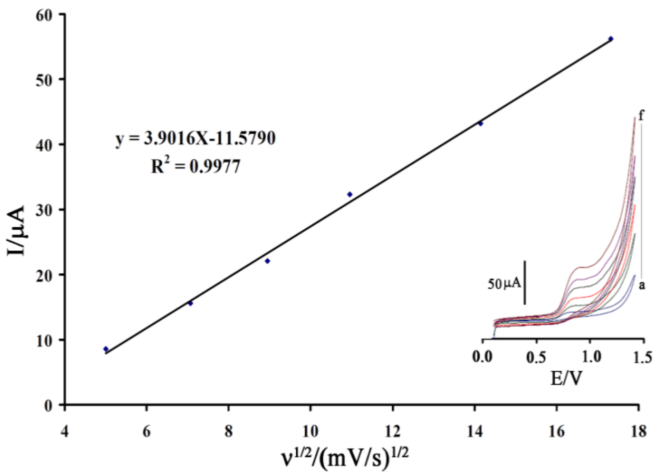


Fig. 4. Variation of anodic peak current *vs.* $v^{1/2}$ for electro-oxidation of 500 μM tyrosine. Insert; cyclic voltammograms of rGO/ZnO-NC/CPE containing 500 μM tyrosine at various scan rates; a-f correspond to 25.0, 50.0, 80.0, 120.0, 200.0 and 300.0 mV s^{-1}, respectively

As can be seen, the anodic current increased from 6.26 µA for CPE to 18.7 µA for rGO/ZnO-NC/CPE in the presence of tyrosine. The current density derived from the square wave voltammograms of 180 µM tyrosine at different electrodes shows in Figure 3 insert. The results show that the presence of rGO/ZnO-NC is causes the increase in electrical conductivity of bare electrode

The effect of scan rate (υ) on the oxidation current of tyrosine was also examined (Figure 4 inset). The results showed a relation between peak current and $\nu^{1/2}$ that confirm a diffusion process for oxidation of tyrosine.

Chronoamperometric investigation was used for determination of diffusion coefficient of tyrosine at a surface of rGO/ZnO-NC/CPE (Figure 5 A). From the resulting slope (figure 5B) and Cottrell equation the mean value of the D was found to be 2.37×10^{-5} cm^2/s.

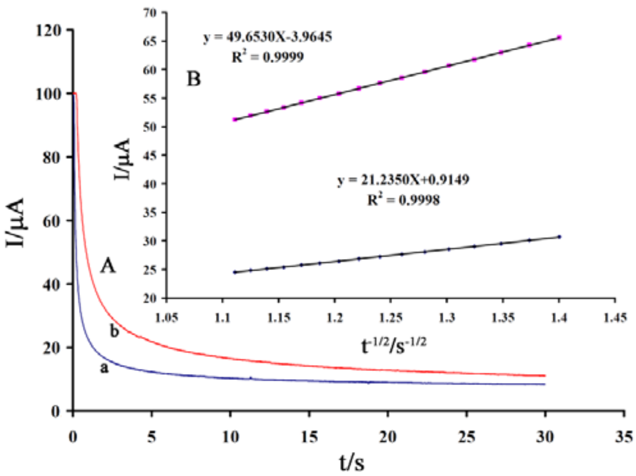


Fig. 5. A) Chronoamperograms obtained at the rGO/ZnO-NC/CPE in the presence of (a) 350 and (b) 500 µM tyrosine at pH 7.4; B) Plots of I *vs*. $t^{-1/2}$ obtained from chronoamperograms

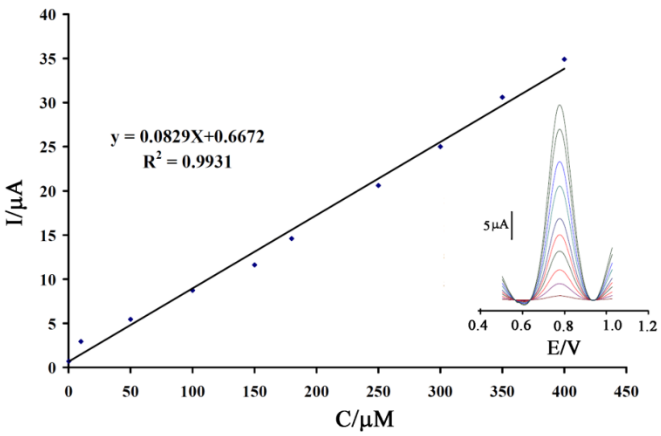


Fig. 6. The plot of oxidation peak current *vs*. tyrosine concentration in the concentration range 0.1-400 µM

3.3. Analysis of tyrosine

Square wave voltammetry (SWV) method was used for study sensitivity of sensor (Figure 6 insert). We detected linear dynamic range between 0.1–400 μM for tyrosine at a surface of rGO/ZnO-NC/CPE (Figure 6). The detection limit was determined at 0.07 μM.

3.4. Interference study

In continuous we check selectivity of rGO/ZnO-NC/CPE for analysis of 20.0 μM tyrosine with acceptable error <5%. The results indicated that the 800-fold of fructose, glucose and alanine, and 650-fold of K^+, Br^-, and 200 fold of thiourea did not effect on tyrosine signal.

3.5. Real sample analysis

We check ability of rGO/ZnO-NC/CPE for analysis tyrosine in biological samples by standard addition method and data are presence in (Table 1). The results confirm ability of rGO/ZnO-NC/CPE for analysis tyrosine in real samples

Table 1. Determination results of tyrosine in real samples (n=3)

Sample	**Added (μM)**	**Expected (μM)**	**Found (μM)**	**Recovery %**
Water	---	---	<Limit of detection	---
	20.00	20.00	19.85±0.97	99.25
Pharmaceutical serum	---	---	<Limit of detection	---
	50.00	50.00	51.05±1.45	102.1

4. CONCLUSIONS

In this research, we synthesized rGO/ZnO-NC by chemical precipitation method and characterized SEM and EDAX methods. In continuous, rGO/ZnO-NC was used for modification of carbon paste electrode. The rGO/ZnO-NC/CPE was used for analysis of tyrosine in the concentration range 0.1-400 μM. The rGO/ZnO-NC/CPE showed good ability for analysis of tyrosine in real samples

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