

*Full Paper*

## **SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub> Nanocomposite Decorated Graphene Modified Carbon Ionic Liquid Electrode as an Electrochemical Sensor for the Determination of Tyrosine**

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**Abstract-** SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>/GR nanocomposite decorated graphene modified carbon ionic liquid electrode (SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>/GR/IL/CPE) was prepared. The electrochemical behavior of tyrosine was studied in 0.1 M phosphate buffer solution (PBS) of pH 7.0 using cyclic voltammetry (CV) while differential pulse voltammetry (DPV) was used for quantification. Under optimum condition, the DPV response offered linear dynamic range for tyrosine in the concentration range 1.0×10<sup>-6</sup> M–8.0×10<sup>-4</sup> M with detection limit 5.0×10<sup>-7</sup> M (S/N=3). The method was successfully applied for determination of tyrosine in real samples.

**Keywords-** Tyrosine, Ionic liquid, SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>/GR nanocomposite, Carbon paste electrode

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### **1. INTRODUCTION**

Amino acids are recognized to be precursors for various significant biological substances [1]. They play a vital physiological functions in all life forms and also important for

numerous medical, cosmetic and other industrial applications. Amino acids are also exciting probe molecules owing to the variety of functional groups that can be found in the same molecule (-COOH, -NH<sub>2</sub>, -OH, -CH<sub>x</sub> etc.) [2]. Tyrosine is a well-recognized as a kind of essential aromatic amino acid and important constituent of protein, plays vital roles in photosynthesis and mammalian central nervous system by virtue of its asymmetric structure and phenol functionality [3]. Tyrosine is barely present in vegetables, hence often added to dietary and food products as well as to the pharmaceutical formulations [4]. Earlier studies have proved the importance of phosphotyrosine levels in controlling and regulating the metabolic stability of acetylcholine receptors in the muscle cells [5]. Maintaining balance in tyrosine level is very important, as tyrosine is an indicator of health status. Its nonexistence could cause hypochondrium, albinism, alkaptonuria, as well as depression and other psychological disorders. In contrast, high concentration of tyrosine promotes Parkinson's disease and increases the chances of sister chromatid exchanges [6]. Thus it is obvious that tyrosine is of great importance in the field of pharmacology, thereby emphasizing the need to monitor it to ensure a healthy and disease-free life style. Other methods for the determination of tyrosine are spectrophotometry, fluorometry, gas chromatography–mass spectroscopy, infrared (IR) optical sensor and ion exchange chromatography [7-11]. However, these methods are less favored as they are expensive, time-consuming, and involve intensive sample preparation. Furthermore, electrochemical analysis is the most suitable means to study tyrosine as it is an electro-active catecholamine [12-19]. Electroanalysis is a very cost effective method with features such as sensitivity, selectivity, specificity and fast response [20-32].

Carbon paste electrode has been used as a working electrode for many biosensor applications because of its simple method of preparation, easy renewability of the surface, compatibility with various types of modifiers, cost effectiveness and, more importantly biocompatibility [33-51]. There have been electroanalytical studies of many materials using conventional bare electrodes without any modification. Unfortunately, these electrodes exhibited poor responses as they succumbed to surface fouling [52-64].

Graphene (GR) has attracted considerable attention in recent years due to physicochemical properties such as large surface area, excellent conductivity and electrocatalytic activities, antifouling ability, high porosity, wide electrochemical window, strong mechanical strength, cheap production and biocompatibility. Decoration of GR by magnetic iron oxide (e.g., magnetite Fe<sub>3</sub>O<sub>4</sub>) nanoparticles, which are very important magnetic materials, can improve optical, magnetic and electrochemical properties of GR [65]. Usually, an inert silica (SiO<sub>2</sub>) nanoparticle coating on the surface of magnetite nanoparticles prevents their aggregation, and improves their chemical stability. In addition, the silica coating enhances the coulomb repulsion of the magnetic nanoparticles [66,67].

Room temperature ionic liquids (RTILs) are either organic salts or mixtures of salts that are fluid at room or near-room temperature. Due to the excellent physicochemical properties of them such as wide electrochemical windows, chemical and thermal stability, high ionic conductivity, negligible vapor pressure, good antifouling ability, inherent catalytic ability and well biocompatibility; they can be used as the modifier or the supporting electrolyte in electroanalysis [68,69].

In the present work, we describe the preparation of a new carbon paste electrode modified with  $\text{SiO}_2@Fe_3O_4/GR$  nanocomposite and ionic liquid ( $\text{SiO}_2@Fe_3O_4/GR/IL/CPE$ ) and investigate its performance for the determination of tyrosine.

## 2. EXPERIMENTAL

### 2.1. Instrumentation and reagents

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302 N, Eco Chemie, the Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. A conventional three electrodes cell was used at  $25 \pm 1$  °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and the  $\text{SiO}_2@Fe_3O_4/GR/IL/CPE$  were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was employed for pH measurements.  $\text{SiO}_2@Fe_3O_4/GR$  nanocomposite was synthesized in our laboratory.

All solutions were freshly prepared with double distilled water. Tyrosine and all other reagents were of analytical grade and were obtained from Merck chemical company (Darmstadt, Germany). The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0-9.0.

### 2.2. Fabrication of modified electrode

The  $\text{SiO}_2@Fe_3O_4/GR/IL/CPE$ s were prepared by hand mixing 0.04 g of  $\text{SiO}_2@Fe_3O_4/GR$  nanocomposite with 0.96 g graphite powder and 0.2 ml ionic liquid with a mortar and pestle. Then, ~0.7 mL of paraffin oil was added to the above mixture and mixed for 20 min until a uniformly-wetted paste was obtained. The paste was then packed into the end of a glass tube (ca. 3.4 mm i.d. and 15 cm long). A copper wire inserted into the carbon paste provided the electrical contact. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing with a weighing paper.

For comparison, unmodified CPE in the absence of both IL and  $\text{SiO}_2@Fe_3O_4/GR$  nanocomposite were also prepared in the same way.

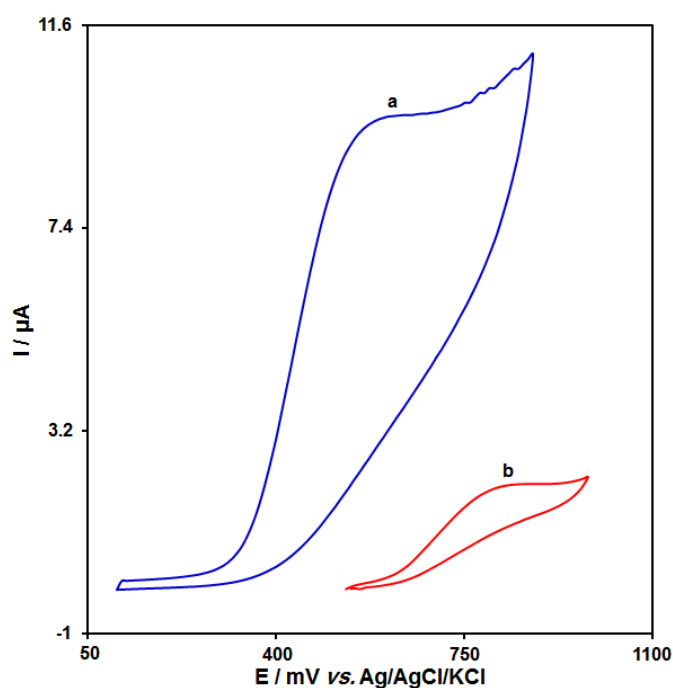
### 2.3. Procedure of real sample preparation

Urine samples were stored in a refrigerator immediately after collection. 10 mL of the sample was centrifuged for 15 min at 2000 rpm. The supernatant was filtered out using a 0.45  $\mu\text{m}$  filter. Then, different volume of the solution was transferred into a 25 mL volumetric flask and diluted to the mark with PBS (pH 7.0). The diluted urine sample was spiked with different amounts of tyrosine.

## 3. RESULTS AND DISCUSSION

### 3.1. Electrochemical properties of $\text{SiO}_2@Fe_3O_4/GR/IL/CPE$

The electrochemical behavior of tyrosine is dependent on the pH value of the aqueous solution. Therefore, pH optimization of the solution seems to be necessary in order to obtain the best electro-oxidation of tyrosine. Thus the electrochemical behavior of tyrosine was studied in 0.1 M PBS in different pH values ( $2.0 < \text{pH} < 9.0$ ) at the surface of  $\text{SiO}_2@Fe_3O_4/GR/IL/CPE$  by CV. It was found that the electro-oxidation of tyrosine at the surface of  $\text{SiO}_2@Fe_3O_4/GR/IL/CPE$  was more favored under neutral conditions than in acidic or basic medium. Thus, the pH 7.0 was chosen as the optimum pH for electro-oxidation of tyrosine at the surface of  $\text{SiO}_2@Fe_3O_4/GR/IL/CPE$ .

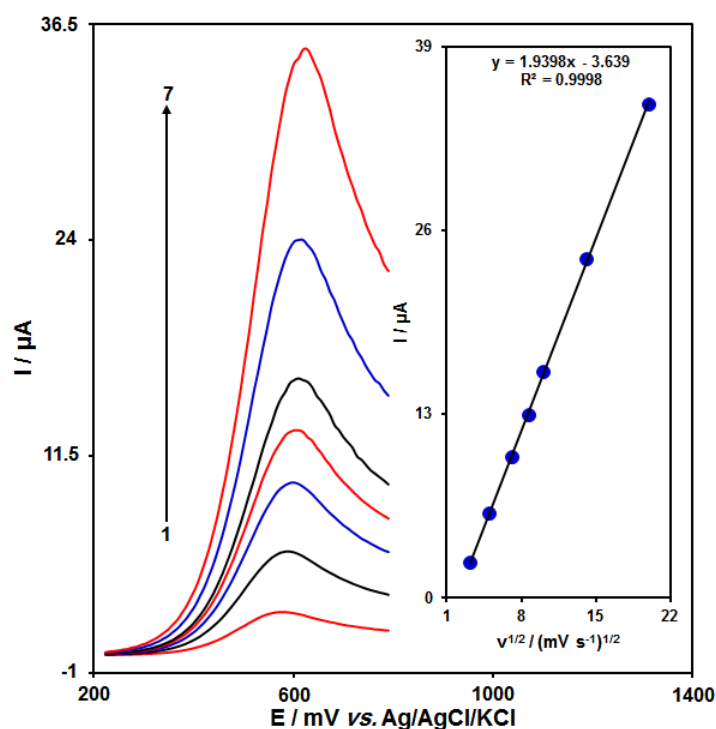


**Fig. 1.** Cyclic voltammograms of (a)  $\text{SiO}_2@Fe_3O_4/GR/IL/CPE$  and (b) unmodified CPE in 0.1 M PBS (pH 7.0) in the presence of 250.0  $\mu\text{M}$  tyrosine at the scan rate  $50 \text{ mVs}^{-1}$

Fig. 1 depicts the cyclic voltammetric responses for the electrochemical oxidation of 250.0  $\mu\text{M}$  tyrosine at  $\text{SiO}_2@Fe_3O_4/\text{GR}/\text{IL}/\text{CPE}$  (curve a) and unmodified CPE (curve b). The anodic peak potential for the oxidation of tyrosine at  $\text{SiO}_2@Fe_3O_4/\text{GR}/\text{IL}/\text{CPE}$  (curve a) is about 600 mV compared with 830 mV for that on the unmodified CPE (curve b).

Similarly, when the oxidation of tyrosine at the  $\text{SiO}_2@Fe_3O_4/\text{GR}/\text{IL}/\text{CPE}$  (curve a) and unmodified CPE (curve b) are compared, an extensive enhancement of the anodic peak current at  $\text{SiO}_2@Fe_3O_4/\text{GR}/\text{IL}/\text{CPE}$  relative to the value obtained at the unmodified CPE (curve b) is observed. In other words, the results clearly indicate that the  $\text{SiO}_2@Fe_3O_4/\text{GR}$  nanocomposite and the ionic liquid improve the tyrosine oxidation signal. These results showed a simple electrochemical oxidation mechanism for oxidation of tyrosine at the surface of  $\text{SiO}_2@Fe_3O_4/\text{GR}/\text{IL}/\text{CPE}$ .

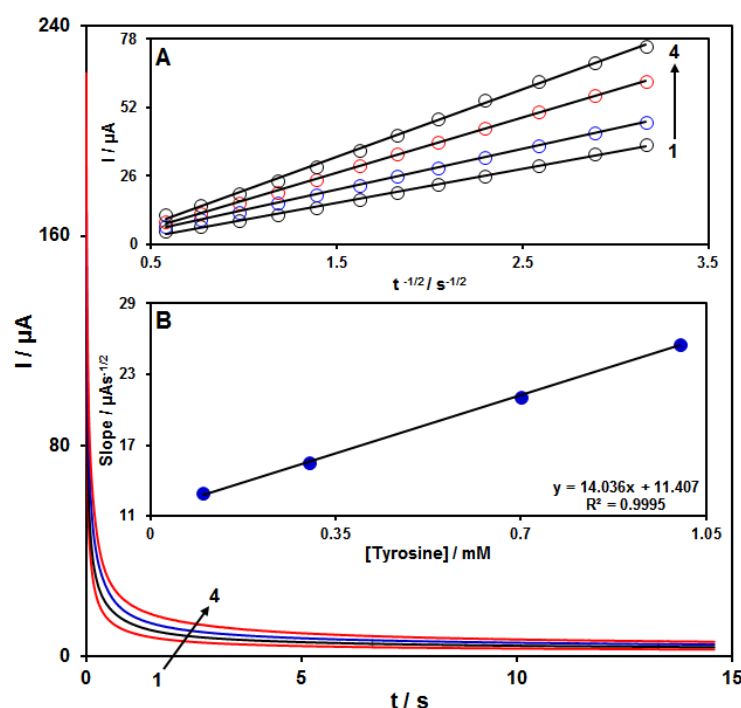
The effect of scan rate on the electro-oxidation of tyrosine at the  $\text{SiO}_2@Fe_3O_4/\text{GR}/\text{IL}/\text{CPE}$  was investigated by linear sweep voltammetry (LSV) (Fig. 2). As can be seen in Fig. 2, the oxidation peak potential shifted to more positive potentials with increasing scan rate, confirming the kinetic limitation in the electrochemical reaction. Also, a plot of peak height ( $I_p$ ) vs. the square root of scan rate ( $v^{1/2}$ ) was found to be linear in the range of 10-400  $\text{mV s}^{-1}$ , suggesting that, at sufficient overpotential, the process is diffusion rather than surface controlled (Fig. 2 inset) [70].



**Fig. 2.** LSVs of  $\text{SiO}_2@Fe_3O_4/\text{GR}/\text{IL}/\text{CPE}$  in 0.1 M PBS (pH 7.0) containing 250.0  $\mu\text{M}$  tyrosine at various scan rates; numbers 1-7 correspond to 10, 25, 50, 75, 100, 200 and 400  $\text{mV s}^{-1}$ , respectively. Inset: Variation of anodic peak current vs.  $v^{1/2}$

### 3.2. Chronoamperometric measurements

Chronoamperometric measurements of tyrosine at  $\text{SiO}_2@Fe_3O_4/GR/IL/CPE$  were carried out by setting the working electrode potential at 0.65 V for the various concentrations of tyrosine in PBS (pH 7.0) (Fig. 3). For an electroactive material (tyrosine in this case) with a diffusion coefficient of  $D$ , the current observed for the electrochemical reaction at the mass transport limited condition is described by the Cottrell equation [70]. Experimental plots of  $I$  vs.  $t^{-1/2}$  were employed, with the best fits for different concentrations of tyrosine (Fig. 3A). The slopes of the resulting straight lines were then plotted vs. tyrosine concentration (Fig. 3B). From the resulting slope and Cottrell equation the mean value of the  $D$  was found to be  $2.0 \times 10^{-6} \text{ cm}^2/\text{s}$ .

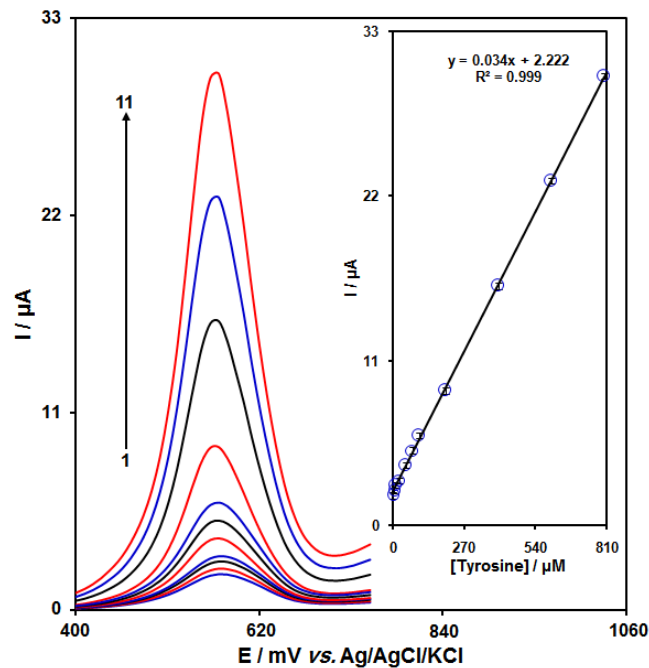


**Fig. 3.** Chronoamperograms obtained at  $\text{SiO}_2@Fe_3O_4/GR/IL/CPE$  in 0.1 M PBS (pH 7.0) for different concentration of tyrosine. The numbers 1–4 correspond to 0.1, 0.3, 0.7 and 1.0 mM of tyrosine. Insets: (A) Plots of  $I$  vs.  $t^{-1/2}$  obtained from chronoamperograms 1–4. (B) Plot of the slope of the straight lines against tyrosine concentration.

### 3.3. Calibration plot and limit of detection

The peak current of tyrosine oxidation at the surface of the modified electrode can be used for determination of tyrosine in solution. Therefore, differential pulse voltammetry (DPV) experiments were done for different concentrations of tyrosine. The oxidation peak currents of tyrosine at the surface of a modified electrode were proportional to the

concentration of the tyrosine within the ranges 1.0 to 800.0  $\mu\text{M}$  (Fig. 4). The detection limit ( $3\sigma$ ) of tyrosine was found to be  $5.0 \times 10^{-7}$  M.



**Fig. 4.** DPVs of  $\text{SiO}_2@Fe_3O_4/GR/IL/CPE$  in 0.1 M (pH 7.0) containing different concentrations of tyrosine. Numbers 1–11 correspond to 1.0, 5.0, 10.0, 25.0, 50.0, 75.0, 100.0, 200.0, 400.0, 600.0 and 800.0  $\mu\text{M}$  of tyrosine. Inset: The plot of the tyrosine peak currents as a function of tyrosine concentration in the range of 1.0–800.0  $\mu\text{M}$

### 3.4. Real sample analysis

In order to evaluate the analytical applicability of the proposed method, also it was applied to the determination of tyrosine in urine sample.

**Table 1.** The application of  $\text{SiO}_2@Fe_3O_4/GR/IL/CPE$  for determination of tyrosine in urine samples ( $n=5$ ). All concentrations are in  $\mu\text{M}$

Sample	Spiked	Found	Recovery (%)	R.S.D. (%)
Urine	0	-	-	-
	5.0	4.9	98.0	10.3
	10.0	10.3	103.0	2.4
	15.0	15.1	100.7	1.7
	20.0	19.8	99.0	2.9

The results for determination of this compound in urine sample are given in Table 1. Satisfactory recovery of the experimental results was found for tyrosine. The reproducibility of the method was demonstrated by the mean relative standard deviation (R.S.D.).

#### 4. CONCLUSIONS

Determination of tyrosine was performed using  $\text{SiO}_2@Fe_3O_4/GR/IL/CPE$  by means of voltammetry. Under the optimum conditions, the oxidation current response of tyrosine was linear in the concentration range of 1.0-800.0  $\mu\text{M}$ . The detection limit of 0.5  $\mu\text{M}$  was achieved for tyrosine. The electrochemical sensor has high sensitivity toward the analyte with a good reproducibility (due to the high synergetic activity of  $\text{SiO}_2@Fe_3O_4/GR$  nanocomposite and ionic liquid).

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