

Full Paper

New Strategy for Determination of Levodopa using Carbon Paste Electrode Modified with SiO₂@Fe₃O₄/GR Nanocomposite, Ionic Liquid and 2-(ferrocenylethynyl)fluoren-9-one

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Abstract- In this study, SiO₂@Fe₃O₄/GR nanocomposite, ionic liquid and 2-(ferrocenylethynyl)fluoren-9-one (2FE) modified carbon paste electrode (SiO₂@Fe₃O₄/GR/2FE/IL/CPE) was used for the determination of levodopa. The electrochemical behavior of levodopa was investigated using cyclic voltammetry (CV), chronoamperometry (CHA) and differential pulse voltammetry (DPV) techniques. Due to the fine characteristics of modified electrode, a good linear relationship between the anodic peak current and levodopa concentration in the range 0.1–500.0 μM was observed. The detection limit (3σ) obtained by DPV was 6.0×10⁻⁸ M (S/N=3). Here, a new sensor is introduced that is simple, rapid, sensitive, selective and cost-effective for quantitation of levodopa in real samples.

Keywords- Levodopa, SiO₂@Fe₃O₄/GR nanocomposite, Ionic liquid, 2-(ferrocenylethynyl)fluoren-9-one, Carbon paste electrode, Voltammetry

1. INTRODUCTION

Levodopa (LD) is the immediate precursor of dopamine. The significant deficiency of dopamine in the brain leads to Parkinson's disease (PD). Dopamine fails to pass the blood-brain barrier, so it cannot be directly injected to replenish the insufficient of dopamine [1]. Levodopa is chosen as a remedial drug for the treatment of PD because it is able to penetrate the blood-brain barrier, convert to dopamine and preferentially accumulate in the striatum [2-4]. However, the auto-oxidization of levodopa occurs in the peripheral system, which can produce serious side effects, such as nausea, vomiting and dyskinesia [5]. Therefore, it is important to develop a simple and precise analytical method for the determination of levodopa in biological fluids. Hitherto, a variety of approaches are reported to detect the level of levodopa such as flow injection analysis, high-performance liquid chromatography (HPLC), capillary electrophoresis and spectrophotometry [6-11]. However, these listed methods have some limits, such as time-consuming, perform sophisticated equipment, and expensive [12-20]. But, electrochemical methods due to the advantages of relatively fast response, simple instrumentation, high sensitivity and selectivity, low cost, facile miniaturization and low power requirement have shown to be a powerful tool [21-35].

Conventionally, mercury electrodes are being used for trace material determinations. However, due to its toxicity, mercury has been restricted for use as an electrode material. This has led to the further discovery of other alternative electrode materials for electroanalytical purposes [36-41]. The purpose of this work was to develop a user friendly, quick response and high accuracy sensor which could be applicable even at ambient conditions for the detection of levodopa, well known for its exceptional health benefits. Chemically modified carbon paste electrodes are more advantageous as they can be easily fabricated, produce low residual current and noise, have good reproducibility, are chemically inert, provide rapid renewal of surface and are most cost effective compared to other electrodes. In addition to these, the modified electrodes are upgraded in their physical and electrocatalytic properties [42-48].

Magnetic Fe_3O_4 nanoparticles (Fe_3O_4 NPs) have attracted considerable interest for biosensor applications because of excellent magnetic responsivity, high density, ease of surface modification and relative large surface area; but these nano-oxides are usually in colloidal forms. Graphene (GR), a new class of two-dimensional carbon nanostructure, has stimulated extremely attention for its unique mechanical, physical, and chemical properties [49, 50]. These properties make GR very promising as a very interesting support for the growth of Fe_3O_4 NPs. In addition, the silica (SiO_2) has been widely used as catalysis, electronic device and amorphous materials. Moreover, it has been successfully used as a carrier for Fe_3O_4 NPs [51,52].

Ionic liquids (ILs) are ionic media resulting from the combination of organic cations and various anions; they are liquids at room temperature and represent a new class of nonaqueous

but polar solvents which are able to dissolve many compounds. In recent years, ILCPEs with such interesting advantages as low cost, ease of preparation, high conductivity, wide electrochemical windows, antifouling effect and renewable surface, have been widely used in the field of electrochemical sensing [53]. These electrodes are prepared by substituting the nonconductive organic binder with highly conductive ionic liquids, which exhibit superior electrochemical performances over the traditional working electrodes [54-56]

Also ferrocene (Fc) and ferrocene-based derivatives have been investigated due to their use as color pigments and as high burning rate catalysts. Therefore they are widely used as modified materials in analytical chemistry, particularly as electron-transfer mediators in electrochemical biosensors [57].

In this study, we describe application of $\text{SiO}_2@Fe_3O_4/GR$ nanocomposite, ionic liquid and 2-(ferrocenylethynyl)fluoren-9-one (2FE) modified carbon paste electrodes ($\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$) for voltammetric determination of levodopa. The proposed sensor showed good electrocatalytic effect on levodopa. $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$ shows advantages in terms of selectivity, reproducibility and sensitivity. Eventually, this new constructed electrochemical sensor was used for determination of levodopa in real samples.

2. EXPERIMENTAL

2.1. Apparatus and chemicals

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 ± 1 °C. An Ag/AgCl/KCl (3.0 M) electrode (Azar Electrode, Urmia, Iran), a platinum wire (Azar Electrode, Urmia, Iran), and the $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$ were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was employed for pH measurements. 2-(ferrocenylethynyl)fluoren-9-one was synthesized as reported previously. $\text{SiO}_2@Fe_3O_4/GR$ nanocomposite was synthesized as reported previously.

All solutions were freshly prepared with double distilled water. Levodopa 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. Preparation of the electrode

The $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$ s were prepared by hand mixing 0.04 g of $\text{SiO}_2@Fe_3O_4/GR$ nanocomposite, 0.01 g of 2FE with 0.95 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 $\text{SiO}_2@Fe_3O_4/GR$ nanocomposite, 2FE and ionic liquid were also prepared in the same way.

2.3. Procedure of real samples 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 μm 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 levodopa.

3. RESULTS AND DISCUSSION

3.1. Electrochemical properties of $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$

To the best of our knowledge there is no prior report on the electrochemical properties and, in particular, the electrocatalytic activity of 2FE in an aqueous media. Therefore, $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$ was prepared and its electrochemical properties were studied in a PBS (pH 7.0) using CV. It should be noted that one of the advantages of 2FE as an electrode modifier is its insolubility in aqueous media. Experimental results showed reproducible and well-defined CVs. Anodic and cathodic peak potentials were 0.35 and 0.25 V vs. $\text{Ag}/\text{AgCl}/\text{KCl}$ (3.0 M) respectively. The observed peak separation potential, $\Delta E_p = (E_{pa} - E_{pc})$ of 100 mV, was greater than the value of $59/n$ mV which is expected for a reversible system [58], suggesting that the redox couple of 2FE in $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$ has a quasi-reversible behavior in aqueous medium [58].

3.2. Electrocatalytic oxidation of levodopa at a $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$

The electrochemical behavior of levodopa is dependent on the pH value of the aqueous solution, whereas the electrochemical properties of Fc/Fc^+ redox couple are independent on pH. Therefore, pH optimization of the solution seems to be necessary in order to obtain the electrocatalytic oxidation of levodopa. Thus the electrochemical behavior of levodopa was studied in 0.1 M PBS in different pH values ($2.0 < \text{pH} < 9.0$) at the surface of $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$ by CV. It was found that the electrocatalytic oxidation of levodopa at the surface of $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$ was more favored under neutral conditions than in acidic or basic medium. This appears as a gradual growth in the anodic

peak current and a simultaneous decrease in the cathodic peak current in the CVs of $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$. Thus, the pH 7.0 was chosen as the optimum pH for electrocatalysis of levodopa oxidation at the surface of $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$.

Fig. 1 depicts the CV responses for the electrocatalytic oxidation of 300.0 μM levodopa at unmodified CPE (curve b) and $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$ (curve d).

As it is seen, the anodic peak potential for levodopa oxidation at the $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$, and unmodified CPE are 350 and 670 mV, respectively. These results indicate that 2FE can act as a good mediator and peak potential for levodopa oxidation at the $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$ shift by ~ 320 mV toward negative values compared to unmodified CPE respectively. However, $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$ shows much higher anodic peak current for the oxidation of levodopa compared to unmodified CPE, indicating that the combination of $\text{SiO}_2@Fe_3O_4/GR$ nanocomposite, ionic liquid and the mediator (2FE) has significantly improved the performance of the electrode toward levodopa oxidation. In fact, $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$ in the absence of levodopa exhibited a well-behaved redox reaction (Fig. 1, curve c) in 0.1 M PBS (pH 7.0). However, there was a drastic increase in the anodic peak current in the presence of 300.0 μM levodopa (curve d), which can be related to the strong electrocatalytic effect of the $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$ towards this compound [58].

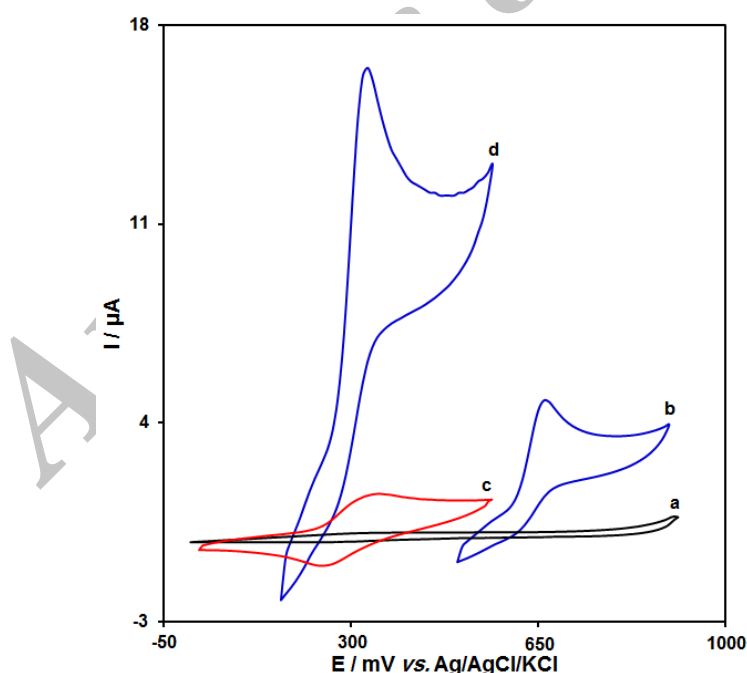


Fig. 1. CVs of (a) unmodified CPE in 0.1 M PBS (pH 7.0) containing 0.3 mM levodopa; (b) unmodified CPE in 0.1 M PBS (pH 7.0) containing 0.3 mM levodopa; (c) $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$ in 0.1 M PBS (pH 7.0); (d) $\text{SiO}_2@Fe_3O_4/GR/2FE/IL/CPE$ in 0.1 M PBS (pH 7.0) containing 0.3 mM levodopa

The effect of scan rate on the electrocatalytic oxidation of levodopa at the $\text{SiO}_2@Fe_3O_4/\text{GR}/2\text{FE}/\text{IL}/\text{CPE}$ 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 5-40 mV s^{-1} , suggesting that, at sufficient overpotential, the process is diffusion rather than surface controlled (Fig. 2) [58].

Fig. 3 illustrates the Tafel plot for the sharp rising part of the LSV at the scan rate of 10 mV s^{-1} . If deprotonation of levodopa is a sufficiently fast step, the Tafel plot can be used to estimate the number of electrons involved in the rate determining step. A Tafel slope of 0.1583 V was obtained which is consistent well with the involvement of one electron in the rate determining step of the electrode process [58], assuming a charge transfer coefficient, α of 0.63.

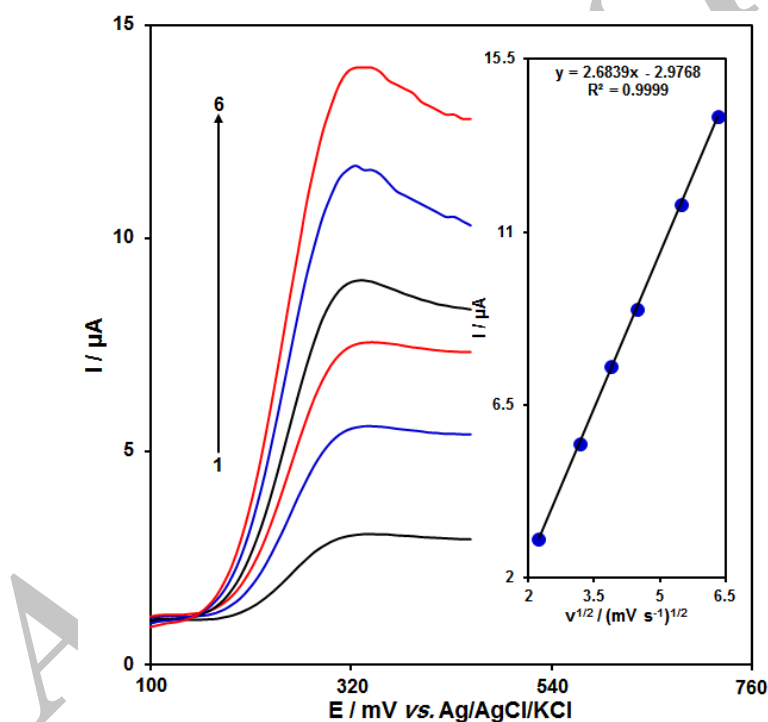


Fig. 2. LSVs for oxidation of 50.0 μM levodopa at the surface of modified electrode at various scan rates; numbers 1-6 correspond to 5, 10, 15, 20, 30 and 40 mV s^{-1} . Inset: Variation of anodic peak current versus the square root of scan rate

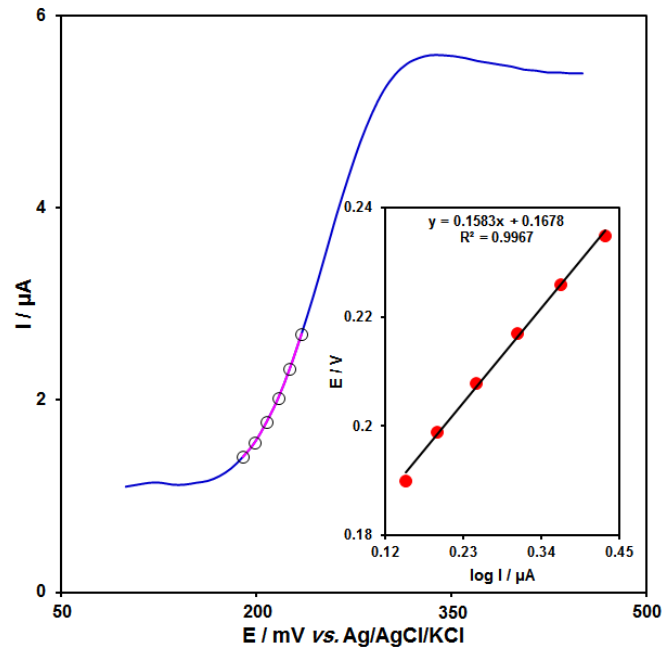


Fig. 3. LSVs (at 10 mV s^{-1}) of electrode in 0.1 M PBS (pH 7.0) containing $50.0 \mu\text{M}$ levodopa. The points are the data used in the Tafel plot. The inset shows the Tafel plot derived from the LSV

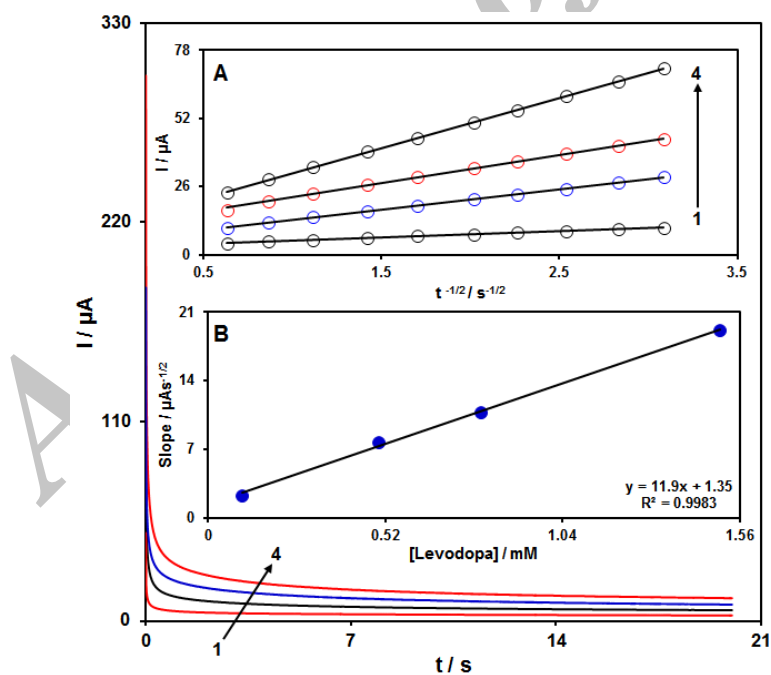


Fig. 4. Chronoamperograms obtained at $\text{SiO}_2@\text{Fe}_3\text{O}_4/\text{GR}/2\text{FE}/\text{IL}/\text{CPE}$ in 0.1 M PBS (pH 7.0) for different concentrations of levodopa. The numbers 1–4 correspond to 0.1, 0.5, 0.8 and 1.5 mM of levodopa. Insets: (A) Cottrell's plot for the data from the chronoamperogram (B) Plot of the slope of the straight lines against levodopa concentration.

3.3. Chronoamperometric measurements

Chronoamperometric measurements of levodopa at $\text{SiO}_2@\text{Fe}_3\text{O}_4/\text{GR}/2\text{FE}/\text{IL}/\text{CPE}$ were carried out by setting the working electrode potential at 400 mV for the various concentrations of levodopa in PBS (pH 7.0) (Fig. 4). For an electroactive material (levodopa 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 [58]. Experimental plots of I vs. $t^{-1/2}$ were employed, with the best fits for different concentrations of levodopa (Fig. 4A). The slopes of the resulting straight lines were then plotted vs. levodopa concentration (Fig. 4B). From the resulting slope and Cottrell equation the mean value of the D was found to be $1.47 \times 10^{-6} \text{ cm}^2/\text{s}$.

3.4. Calibration plot and limit of detection

DPV method was used to determine the concentration of levodopa (Fig. 5). The plot of peak current vs. levodopa concentration consisted of linear segment with slope of $0.043 \mu\text{A} \mu\text{M}^{-1}$ in the concentration ranges of 0.1 to $500.0 \mu\text{M}$.

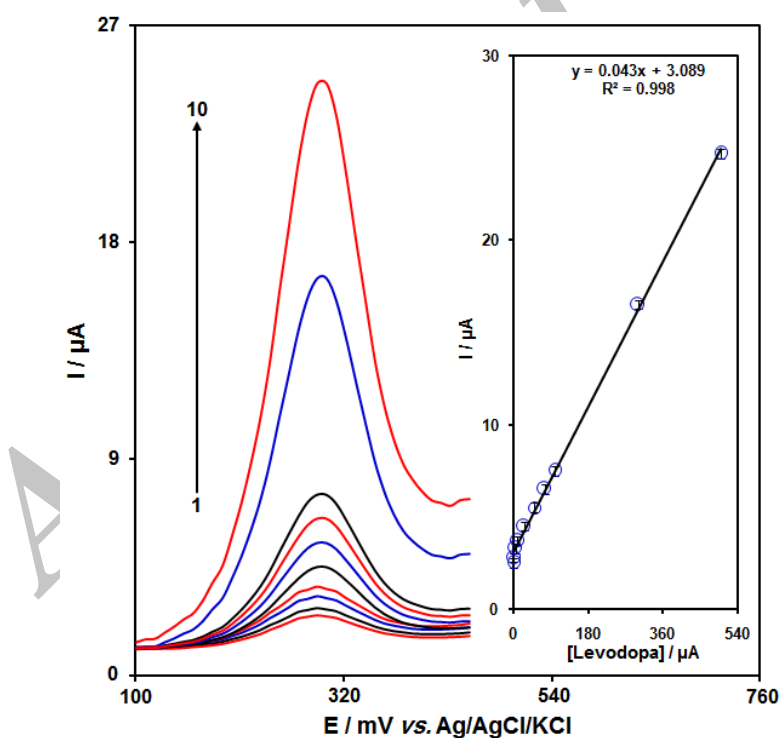


Fig. 5. DPVs of $\text{SiO}_2@\text{Fe}_3\text{O}_4/\text{GR}/2\text{FE}/\text{IL}/\text{CPE}$ in 0.1 M (pH 7.0) containing different concentrations of levodopa. Numbers 1–10 correspond to 0.1, 1.0, 5.0, 10.0, 25.0, 50.0, 75.0, 100.0, 300.0 and $500.0 \mu\text{M}$ of levodopa. Inset: Plot of the electrocatalytic peak current as a function of levodopa concentration in the range of 0.1– $500.0 \mu\text{M}$

The detection limit (3σ) of levodopa was found to be 0.06 μM . These values are comparable with the values obtained previously for determination of levodopa (Table 1).

Table 1. Comparison of efficiency of some modified electrodes in the electrochemical determination of levodopa

Electrode	Modifier	Method	LDR (M)	LOD (M)	Ref.
Carbon Paste	Meso-tetrakis(3-methylphenyl) cobalt porphyrin (CP) and TiO ₂ nanoparticles	Voltammetry	1.0×10^{-6} – 1.0×10^{-4}	6.9×10^{-8}	[12]
Carbon Paste	Graphene nanosheets and 1-(4-bromobenzyl)-4-ferrocenyl-1H-[1,2,3]-triazole	Voltammetry	5.0×10^{-8} – 8.0×10^{-4}	1.5×10^{-8}	[13]
Graphite Screen Printed	Graphene Oxide/ZnO	Voltammetry	1.0×10^{-6} – 1.0×10^{-3}	4.5×10^{-7}	[19]
Carbon Paste	SiO ₂ @Fe ₃ O ₄ /GR nanocomposite, ionic liquid and 2-(ferrocenylethynyl)fluoren-9-one	Voltammetry	1.0×10^{-7} – 5.0×10^{-4}	6.0×10^{-8}	This work

3.5. Real sample analysis

In order to evaluate the analytical applicability of the proposed method, also it was applied to the determination of levodopa in urine samples. The results for determination of levodopa in real samples are given in Table 2. Satisfactory recovery of the experimental results was found for levodopa. The reproducibility of the method was demonstrated by the mean relative standard deviation (R.S.D.).

Table 2. The application of SiO₂@Fe₃O₄/GR/2FE/IL/CPE for determination of levodopa in urine samples (n=5). All concentrations are in μM

Sample	Spiked	Found	Recovery (%)	R.S.D. (%)
Urine	0	-	-	-
	10.0	10.3	103.0	1.9
	20.0	19.9	99.5	3.2
	30.0	29.2	97.3	2.4
	40.0	40.5	101.2	2.7

4. CONCLUSIONS

The results showed that the oxidation of levodopa was catalyzed by SiO₂@Fe₃O₄/GR nanocomposite, ionic liquid and 2-(ferrocenylethynyl)fluoren-9-one (2FE) in neutral environment and that the peak potential of levodopa was shifted to 0.35 V. Significantly electrochemical response to trace levodopa on SiO₂@Fe₃O₄/GR/2FE/IL/CPE has been observed. Compared with the levodopa oxidation-based levodopa sensor reported previously, this method exhibited wider linear range and lower detecting limit. This sensor proved to be successfully used for levodopa determination in real samples.

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