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A Nanocomposite Material Based on Carbon Nanotubes and $Fe_3O_4@SiO_2$ for the High Selective and Sensitive Electrochemical Determination of Norepinephrine

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An electrochemical sensor was prepared by modifying a graphite screen printed electrode (SPE) with a nanocomposite of magnetic $Fe_3O_4@SiO_2$ nanocomposite and carbon nanotubes (CNTs) for the determination of norepinephrine (NE). Compared with a bare SPE, the $Fe_3O_4@SiO_2$/CNTs/SPE highly enhanced the current response for NE. A linear plot was obtained for current responses versus the concentrations of NE in the range of 0.5 to 400.0 μM with a detection limit of 0.2 μM.

Keywords: Norepinephrine, Carbon nanotubes, $Fe_3O_4@SiO_2$ nanocomposite, Graphite screen printed electrode

1. INTRODUCTION

Norepinephrine (NE), also called noradrenaline (NA) is a crucial catecholamine neurotransmitter in the mammalian central nervous system. Unfortunately, the usefulness of NE is limited by a range of serious side effects, including hypertension, hyperglycemia, nervousness and sweating [1-3]. In addition, extremely abnormal concentrations of NE may lead to the occurrence of a variety of diseases, such as ganglia neuroblastoma, ganglion neuronal, Parkinson's and paraganglioma disease. Also, NE accelerates human immunodeficiency virus-1 (HIV-1) replication via protein kinase [4]. Therefore, the detection of trace amounts of NE in biological fluids gives valuable information in clinical medicine [5]. Various methods are available for the determination of NE including spectrophotometry, capillary electrophoresis, fluorometry, high performance liquid chromatography (HPLC) and electrochemical methods [6-15].

The modification of electrodes has been applied to many sorts of carbon. Great progression have been achieved in the recent years in the field of graphite screen printed carbon electrodes (SPEs) because of allowing the mass production of economical, disposable, reproducible devices and their miniaturized size [16-17].

Recent studies have shown that nanocomposite can be a great choice of substrate in sensors design, enabling to achieve better analytical performances [18-45].

Magnetic Fe_3O_4 nanoparticles have excellent magnetic responsivity and high density that can affect their adsorptive properties. Recently, this condition has led to a growing interest in the synthesis and the application of novel modifier by loading Fe_3O_4 NPs on another solid. Carbon nanotubes (CNTs) can be used as a good support during the growth of Fe_3O_4 NPs. As SiO_2 is the most abundant substance found in the crust of the earth, it has been widely used as catalysis, electronic device and amorphous materials. Forasmuch as SiO_2 shell can enhance the storage stability and can improve the dispersibility of the nanoparticles in solution, it is worth mentioning that SiO_2 has stimulated great attention as sensing material in the design of biosensors. As a result, Fe_3O_4@SiO_2/CNT nanocomposite with a large surface area, low density and good magnetic characteristics can provide great potential application to modified electrode [46-49].

In the present study, a SPE was modified with a nanocomposite of CNTs and Fe_3O_4@SiO_2 nanocomposite for the determination of NE and used for determination of NE in real samples.

2. EXPERIMENTAL

2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands). The screen-printed electrode (Drop Sens, DRP-110, Spain) consists of three main parts which are a graphite counter electrode, a silver pseudo-reference electrode and a graphite working electrode. NE and all other reagents were of analytical grade and were obtained from Merck chemical company (Darmstadt, Germany).

2.2. Preparation of modified electrode

The bare graphite screen printed electrode was coated with Fe_3O_4@SiO_2/CNTs as follows. 2 µl aliquot of the Fe_3O_4@SiO_2/CNTs/H_2O suspension solution (1mg/mL) was casted on the carbon working electrodes, and waiting until the solvent evaporation in room temperature.

2.3. Preparation of real samples

One milliliter of a NE ampoule was diluted to 10 mL with 0.1 M PBS (pH 7.0); then, different volume of the diluted solution was transferred into each of a series of 25 mL volumetric flasks and diluted to the mark with PBS. The NE content was analyzed by the proposed method using the standard addition method.

Urine samples were stored in a refrigerator immediately after collection. Ten milliliters 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 NE.

3. RESULT AND DISCUSSION

3.1. Electrochemical oxidation of NE at a Fe_3O_4@SiO_2/CNTs/SPE

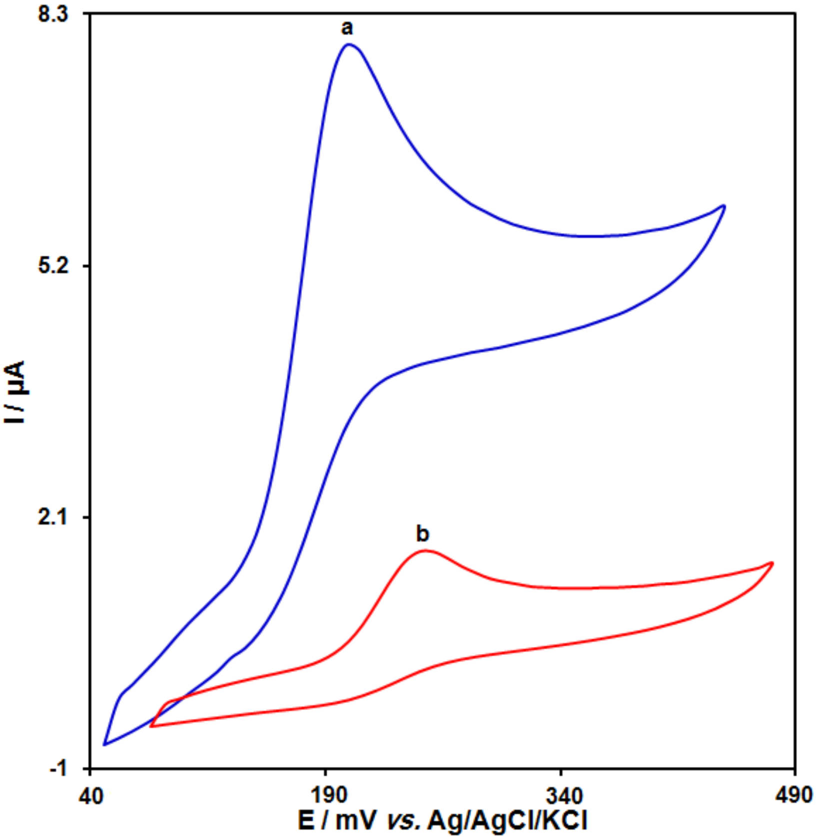


Figure 1. CVs of (a) Fe_3O_4@SiO_2/CNTs/SPE and (b) bare SPE in PBS in the presence of 200.0 µM NE at the scan rate 50 mVs^{-1}.

Fig. 1 depicts the cyclic voltammetric responses for the oxidation of 200.0 µM NE at Fe_3O_4@SiO_2/CNTs/SPE (curve a) and bare SPE (curve b). The anodic peak potential for the oxidation of NE at Fe_3O_4@SiO_2/CNTs/SPE (curve a) is about 200.0 mV compared with 250.0 mV for that on the bare SPE (curve b). Similarly, enhancement of the anodic peak current at Fe_3O_4@SiO_2/CNTs/SPE is observed relative to the value obtained at the bare SPE (curve b). In other words, the results clearly indicate that the combination of CNTs and Fe_3O_4@SiO_2 nanocomposites improve the NE oxidation signal.

3.2. Effect of scan rate

The effect of potential sweep rates on the oxidation current of NE has been studied (Fig. 2). The results showed that the oxidation process is diffusion controlled.

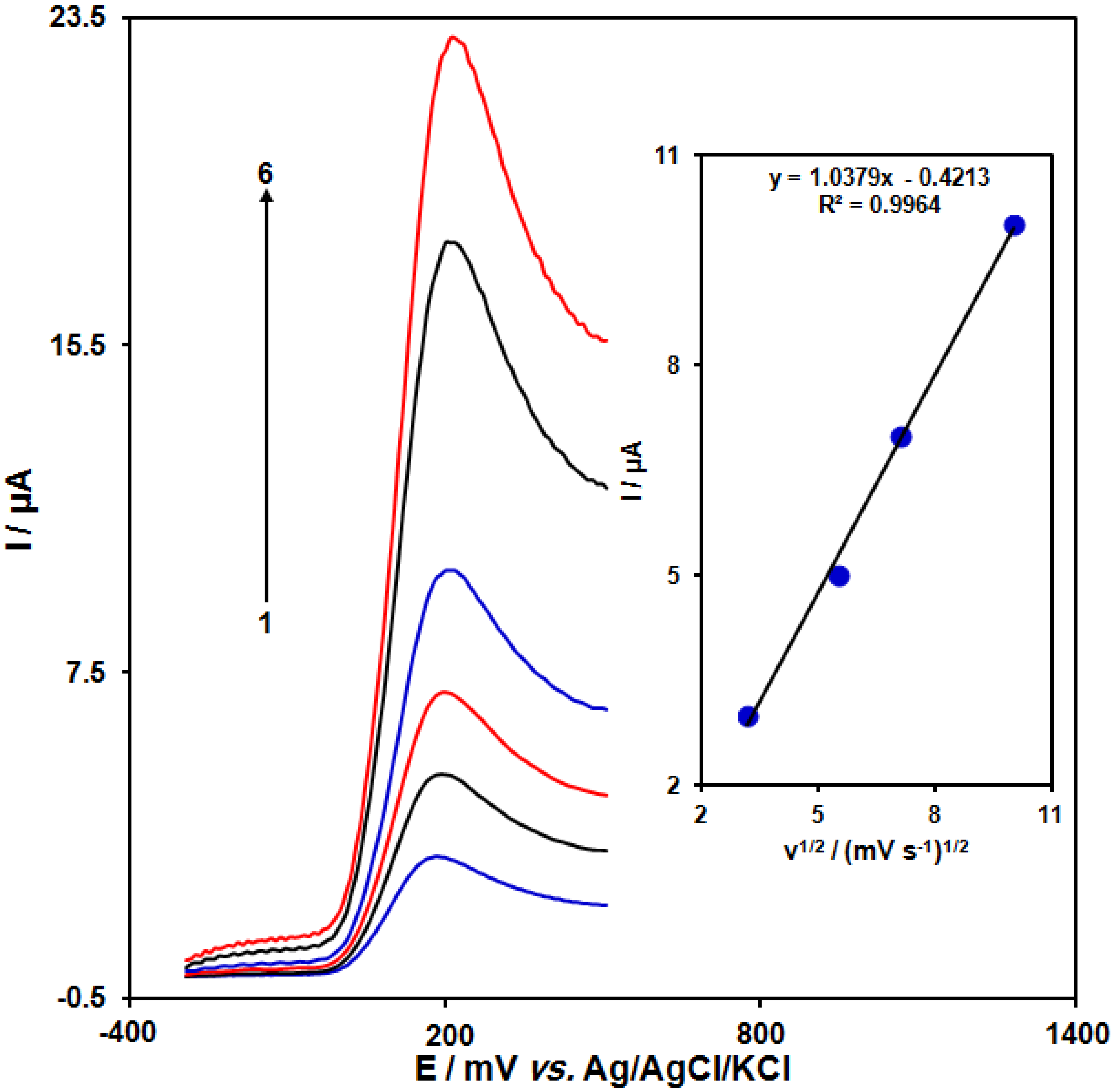


Figure 2. LSVs of Fe_3O_4@SiO_2/CNTs/SPE in PBS containing 150.0 μM NE at 1) 10.0, 2) 30.0, 3) 50.0, 4) 100.0, 5) 300.0 and 6) 500.0 mV s^{-1}. Inset: Variation of anodic peak current *vs.* square root of sweep rate.

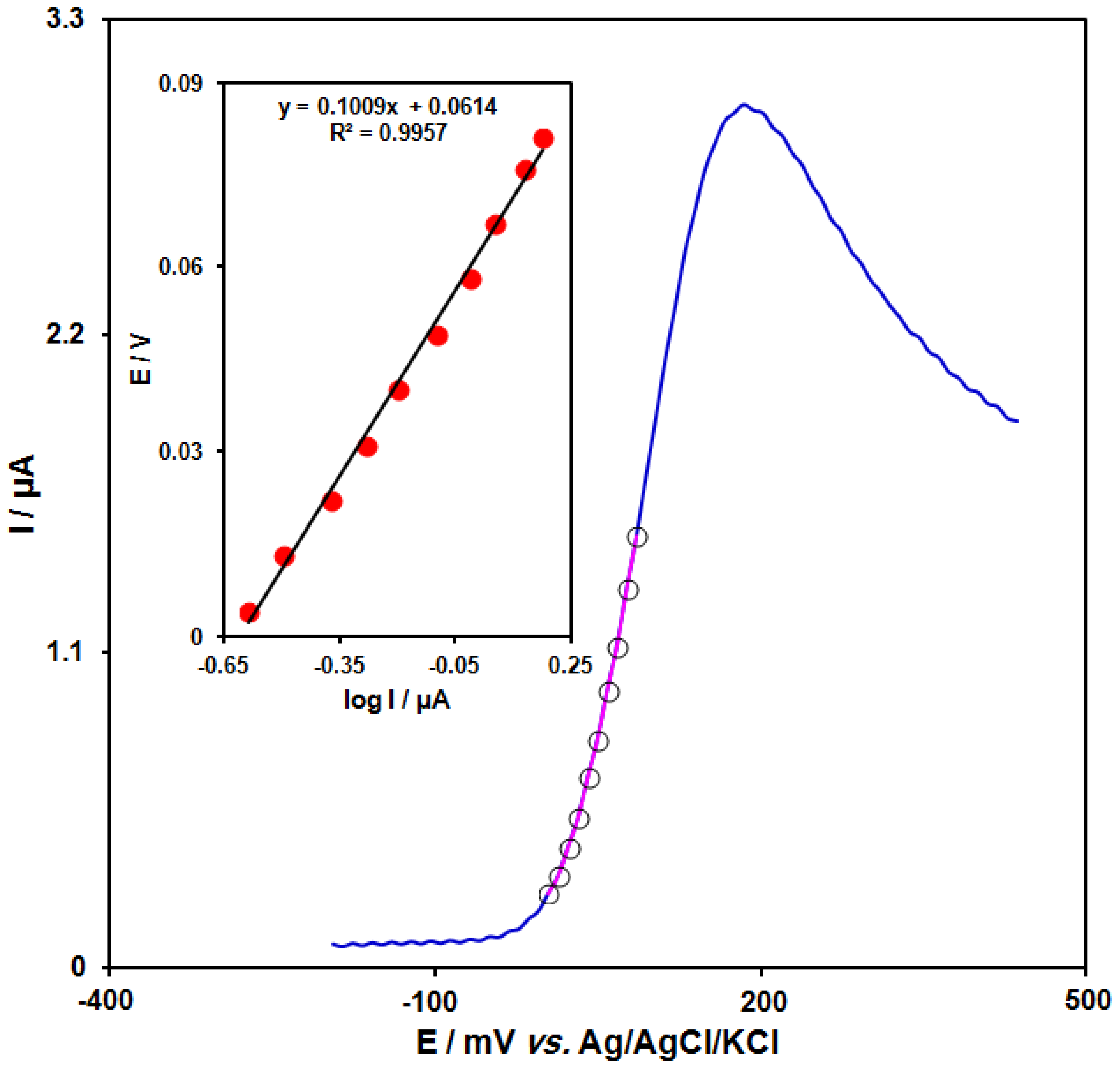


Figure 3. LSV (at 10 mV s^{-1}) of a Fe_3O_4@SiO_2/CNTs/SPE in PBS containing 150.0 µM NE. The inset shows the Tafel plot derived from the LSV.

Fig. 3 shows the LSV of a Fe_3O_4@SiO_2/CNTs/SPE in the presense of 150.0 µM NE, with a sweep rate of 10 mV s^{-1}. The Tafel slope of 0.1009 V decade $^{-1}$ and a charge transfer coefficient of α=0.41 was obtained.

3.3. Chronoamperometric measurements

Chronoamperometric measurements of NE at Fe_3O_4@SiO_2/CNTs/SPE were carried out by setting the working electrode potential at 0.23 V vs. Ag/AgCl/KCl (3.0 M) for the different concentrations of NE (Fig. 4). Using Cottrell equation [50] the mean value of the D was found to be 1.2×10^{-5} cm^2/s.

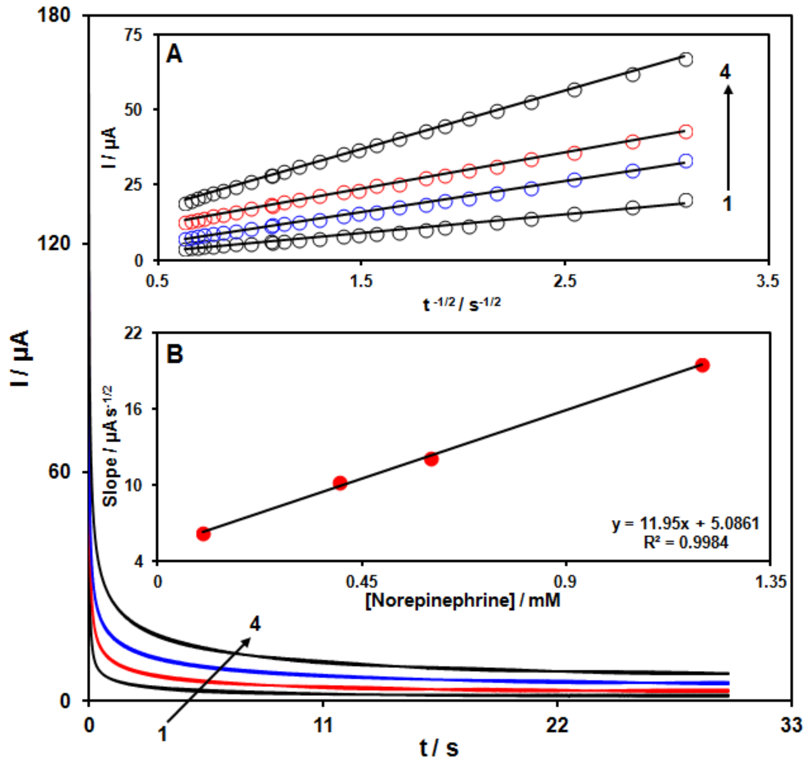
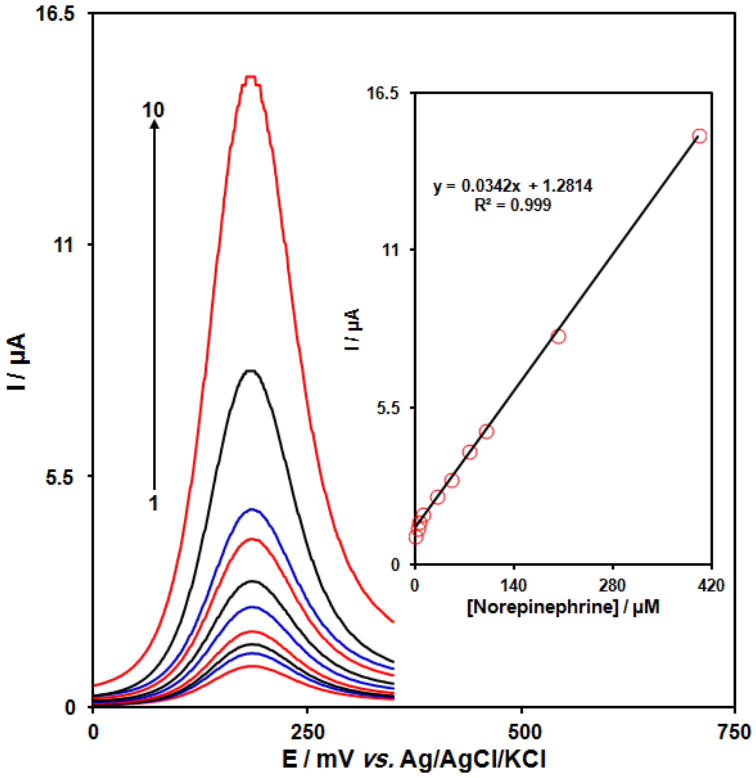


Figure 4. Chronoamperograms obtained at Fe_3O_4@SiO_2/CNTs/SPE in PBS containing different concentration of NE: 1) 0.1, 2) 0.4, 3) 0.6 and 4) 1.2 mM. Insets: (A) Plots of I vs. $t^{-1/2}$. (B) Plot of the slope of the straight lines against NE concentration.



3.4. Calibration plot and limit of detection

SWV experiments were done for different concentrations of NE (Fig. 5). The currents were proportional to the concentration of the NE within the range 5.0×10^{-7} to 4.0×10^{-4} M with detection limit (3σ) of 2.0×10^{-7} M. These values are comparable with values reported by other research groups for oxidation of NE (see Table 1).

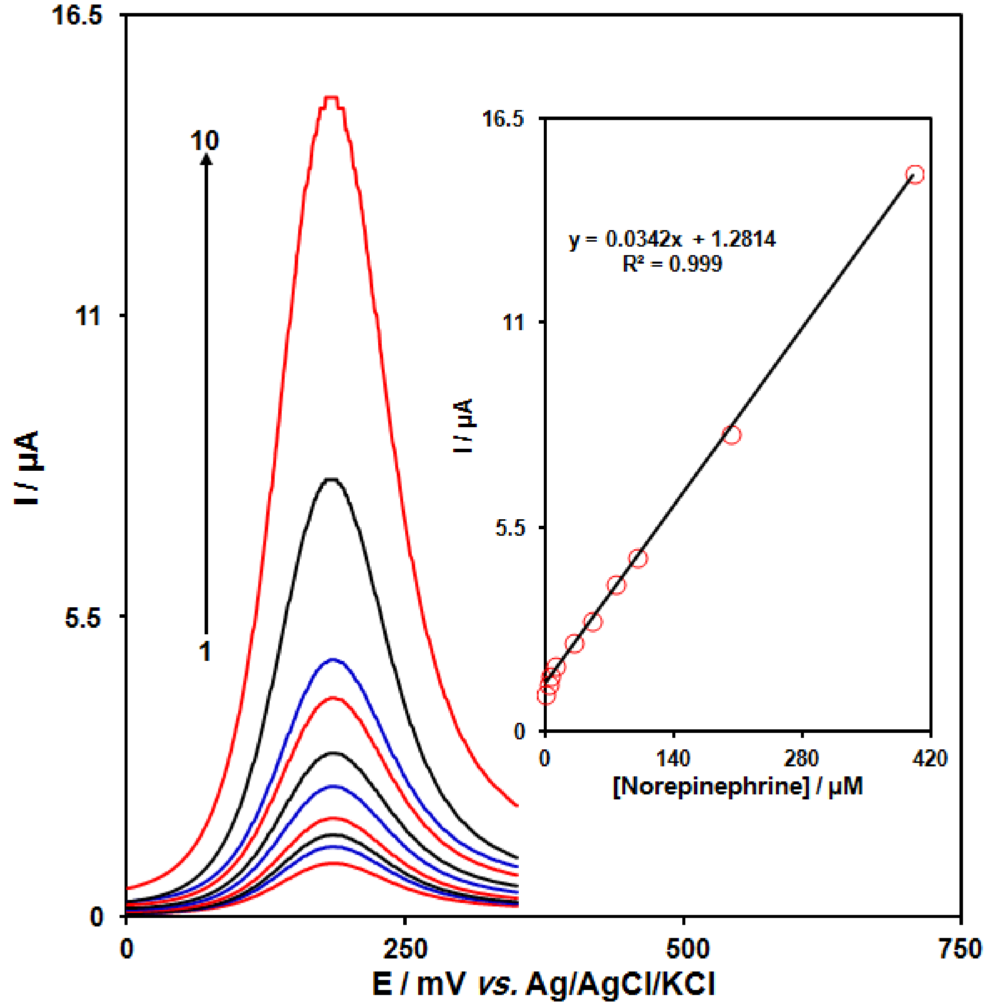


Figure 5. SWVs of $Fe_3O_4@SiO_2$/CNTs/SPE in PBS containing different concentrations of NE: 1) 0.5, 2) 2.5, 3) 5.0, 4) 10.0, 5) 30.0, 6) 50.0, 7) 75.0, 8) 100.0, 9) 200.0 and 10) 400.0 µM. Inset: shows the plots of the peak current as a function of NE concentration.

3.5. Real sample analysis

The developed sensor was applied to the determination of NE in NE ampoule and urine samples. The results are given in Table 2.

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

Electrode	Modifier	LOD	LDR	Ref.
Glassy carbon	Gold nanoparticles/multi-walled carbon nanotubes	0.03 μM	0.2-100.0 μM	51
Glassy carbon	$FeMoO_4$ nanorods	3.7 nM	0.05 - 200.0 μM	52
Glassy carbon	Molecularly imprinted polymer	0.1 μM	0.5- 80.0 μM	53
Glassy carbon	MWNTs-ZnO/chitosan composites	0.2 μM	0.5- 30.0 μM	54
Glassy carbon	Graphene	67.44 nM	0.005- 0.5 μM	55
Glassy carbon	$CdTe@SiO_2$ QDs	9.0 nM	0.08-20.0 μM	56
Glassy carbon	Graphene	6.0×10^{-7} M	6.0×10^{-7}-1.2×10^{-4} M	57
Carbon Nanotubes Paste	Ionic Liquid	0.08 μM	0.2–500 μM	58
Carbon Paste	Carbon nanotube and EBNBH	0.082 μM	0.1-1100.0 μM	59
Glassy carbon	Ag-poly aminosulfonic acid composite	5.66×10^{-8} M	8.49×10^{-7}-7.55×10^{-6} M	60
Carbon Paste	Chloranile	11.2 nM	0.03- 500 μM	61
Screen printed	Carbon Nanotubes/ $Fe_3O_4@SiO_2$ nanocomposite	0.2 μM	0.5-400.0 μM	This work

Table 2. Determination of NE in NE ampoule and urine samples. All the concentrations are in μM (n=5).

Sample	Spiked	Found	Recovery (%)	R.S.D. (%)
NE ampoule	0.0	5.0	-	3.4
	2.5	7.4	98.7	2.7
	5.0	10.1	101.0	3.1
	10.0	15.5	103.3	1.9
	15.0	19.8	99.0	2.8
Urine	0.0	-	-	-
	7.5	7.6	101.3	1.9
	12.5	12.3	98.4	3.2
	17.5	17.1	97.7	2.7
	22.5	23.2	103.1	2.2

4. CONCLUSION

A selective determination of NE has been carried out using a voltammetric sensor prepared by modifying graphite screen printed electrode (SPEs) with carbon nanotubes and $Fe_3O_4@SiO_2$

nanocomposite. The proposed electrode presented high electrocatalytic activity, improved voltammetric behavior and enhancement in the current response of NE. It was shown that the current response was linear with concentration over the range from 0.5 to 400.0 μM.

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