

RESEARCH PAPER

Electrochemical Analysis of Tryptophan using a Nanostructuring Electrode with Multi-walled Carbon Nanotubes and Cetyltrimethylammonium bromide Nanocomposite

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) were immobilized on the surface of a glassy carbon electrode (GCE) in the presence of cetyltrimethylammonium bromide (CTAB) to form a MWCNTs-CTAB nanocomposite-modified electrode. The electrocatalytic response of the modified electrode towards tryptophan (Trp) was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The surface morphology of the modified electrode was characterized by scanning electron microscopy. Under the optimized conditions, a significant electrochemical improvement was observed toward the electrooxidation of tryptophan on the modified electrode surface relative to the unmodified electrode. The limit of detection of $1.6 \mu\text{mol L}^{-1}$ ($S/N = 3$) and linear calibration range of $4.9 - 64.1 \mu\text{mol L}^{-1}$ was obtained for tryptophan determination using a differential pulse voltammetric method in phosphate buffer (0.1 M, pH 3.0). Real sample studies were carried out in human blood serum, which offered good recovery (94.1-104.08%). The electrode showed excellent reproducibility, selectivity and antifouling effects.

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INTRODUCTION

Tryptophan (Trp) is an essential amino acid required for the biosynthesis of proteins (precursor molecules of hormones, neurotransmitters and other relevant bio-molecules) and finds importance in nitrogen balance and the maintenance of muscle mass and body weight in humans [1]. To correct possible dietary deficiencies, Trp is added to dietary and food products as a food fortifier and to pharmaceutical formulations. However, when improperly metabolized, Trp creates a waste product in the brain that is toxic, causing hallucinations and delusions. So, it is necessary to develop an analytical assay for determination of Trp in food, pharmaceutical products and biological fluids. In comparison with other

potential methods, the electrochemical technique exhibits its predominance for the materials with electrochemical activity due to the advantages such as rapid response, low-cost and high sensitivity.

Direct oxidation of Trp on ordinary carbon electrodes, however, is kinetically slow and accompanied by large overpotentials and small oxidation currents. To overcome these obstacles, modification of the electrode surface is an approach to enhance the rate of electron transfer and minimize its overpotential. Despite so much modified electrodes, [2-21] a literature survey confirms that effort about the preparation of new patterns for electrocatalytic oxidation of Trp is still in progress.

The modification of electrodes using multi-

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walled carbon nanotubes (MWCNTs) to design new analytical sensors has been prevalently reported [22, 23]. Homogenous and consistent coating of CNTs on the surface of the electrodes can be attained by simple and low cost followed by the uniform dispersing of electrically charged CNTs [24]. The previous investigations reported that the CNTs have been negatively or positively charged by carboxylic or amino functionalization which helps disperse individual CNTs in the suspension for electrodeposition process [25, 26]. Also several studies have surveyed the electrodeposition of the combination of CNTs/metal ions or CNTs/metal oxides on the surface of various electrode substrates [27-30]. Another appropriate and simple method to overcome the poor solubility of CNTs to attain the stable dispersion is the application of surfactants. In this procedure, the surfactant is adsorbed on the surface of CNTs, and subsequent ultrasonication of the solution, which takes several minutes, will cleave apart their aggregations and debundle nanotubes by steric or electrostatic repulsions resulted from the charge of surfactant hydrophilic groups [31-33].

In this paper, Multi-walled carbon nanotubes were immobilized on the surface of a glassy carbon electrode in the presence of cetyltrimethylammonium bromide to form a MWCNTs-CTAB nanocomposite-modified electrode. Herein, we reported an electrochemical sensor based on MWCNTs-CTAB nanocomposite for determination of tryptophan. The MWCNTs-CTAB nanocomposite modified glassy carbon electrode was fabricated by simple casting technique. Effective parameters on response of the proposed sensor were investigated in details. Finally, the sensor was used for determination of tryptophan in human serum samples.

MATERIALS AND METHODS

Reagents

All chemicals used in this study were of analytical grade from Merck (otherwise those stated) and used without further purification. Multi-walled carbon nanotubes (MWCNTs) (> 95% purity, 10–20 nm diameter, 5–15 nm length) were purchased from Neutrino (Iran–Tehran).

Phosphate buffer solutions (PBS, 0.1 mol L⁻¹) at various pH values were prepared from phosphoric acid, NaH₂PO₄, Na₂HPO₄ and Na₃PO₄·7H₂O and addition of NaOH (1.0 mol L⁻¹) or HCl (1.0 mol L⁻¹) in order to obtain the desired pH value. Double-distilled water was used throughout the study.

Apparatus

Electrochemical experiments were performed using an AUTOLAB modular electrochemical system (Eco Chem. Utrecht, The Netherlands) equipped with PGSTAT-12 model and driven by GPES 4.9 software. A conventional three-electrode cell was used with an Ag/AgCl/KCl (3 mol L⁻¹) as reference electrode, a Pt wire as counter electrode and a modified glassy carbon electrode (GCE) as working electrode. The SEM experiment was made on a XL-30 scanning electron microscope.

Preparation of the modified electrode

5 mg of MWCNTs was added to 5 mL of 2.5 mmol L⁻¹ CTAB aqueous solution. The mixture was sonicated for 35 min to obtain a modifier suspension, which was recorded as MWCNTs-CTAB. Before modification, the GCE was carefully polished on a fine microcloth successively with 0.3 and 0.05 μm alumina slurry until a mirror-shine surface was obtained, and then rinsed with water. A sonication step was performed consecutively in 1:1 HNO₃ and acetone, and water for 10 min, and finally dried at room temperature.

Then, 5 μL prepared MWCNTs-CTAB suspension was dropped on the surface of the cleaned electrode, and dried in air at the room temperature to form MWCNTs-CTAB nanocomposite film on electrode surface (MWCNTs-CTAB/GCE).

Preparation of real samples

Healthy blood serum samples were obtained from Pastor Laboratory (Khoy– Iran) and were stored frozen before use. In order to obtain the proper sample, methanol (2 mL) was added to 1.5 mL of serum sample for protein separation. After vortexing of the serum sample for 2 min, the precipitated proteins were separated by centrifugation (3 min at 5000 rpm). The clear supernatant layer was filtered through 0.45 μm milli-pore filter, and its volume was adjusted to 10 mL using PBS (0.1 mol L⁻¹, pH 3.0). The standard addition method was used for the determination of Trp in serum samples.

RESULTS AND DISCUSSION

Characterization of the prepared electrode

The typical morphologies of the bare GCE (Fig. 1A), MWCNTs/GCE (Fig. 1B) and MWCNTs-CTAB/GCE (Fig. 1C) were characterized by scanning electron microscope. As expected, MWCNTs layer on GCE produces a number of randomly-

tangled spaghetti-like CNTs forming stereo-porous interspaces and a subtle tubule structure of the CNTs (Fig. 1B). The whole assembly on electrode surface (MWCNTs-CTAB) is shown in image C. The surface morphology was changed and gave clear evidence for the successful fabrication of MWCNTs-CTAB on the surface of GCE.

The Fourier transform infrared (FT-IR) spectra provide information regarding the changes in surface functional group of the samples. The FT-IR spectra of the MWCNTs and MWCNTs-CTAB were given in Fig. 2. The peak at 3431 cm^{-1} arose from the hydroxyl group ($-\text{OH}$) stretching vibration

of adsorbed water. The FT-IR spectra of oxidized MWCNTs showed a peak intensity at 1706 cm^{-1} ($\text{C}=\text{O}$ stretching) and 1157 cm^{-1} ($\text{C}-\text{O}$ stretching). The band at 1550 cm^{-1} was the characteristic graphite structure peak, which was assigned to the $\text{C}=\text{C}$ groups of the MWCNTs. These results comparable with those reported in literatures [34,35]. The FT-IR spectra of MWCNTs-CTAB contained bands at 3431 cm^{-1} arises from the stretching vibration of hydroxyl groups. The small absorptions at 2900 and 2833 cm^{-1} are caused by the $\text{C}-\text{H}$ stretching vibration of methyl and methylene groups of CTAB. Moreover, the FT-IR spectra of MWCNTs allied with CTAB showed the reduction in $\text{C}=\text{O}$, $\text{C}-\text{O}$ stretching and $\text{C}=\text{C}$ groups of MWCNTs-CTAB spectrum at 1706 , 1157 and 1550 cm^{-1} , respectively, which designated the utilization of $-\text{COOH}$ of MWCNTs by co-precipitation with CTAB.

Electrochemical behavior of Trp on MWCNTs-CTAB/GCE

Fig. 3 shows the cyclic voltammetry (CV) curves of Trp at bare GCE (curve a) and MWCNTs-CTAB/GCE (curve b), respectively. As can be seen, at the bare GCE, Trp shows a sluggish and much smaller anodic peak response at 0.920 V . While, at the MWCNTs-CTAB/GCE, Trp exhibits a sharp and strong oxidation peak at 0.880 V with greatly increased peak current response, which is 3.7-fold increase in comparison with that at the bare GCE. The negatively shifted oxidation peak potential and 3.7-fold increase in peak current at the MWCNTs-CTAB/GCE indicate that the good catalytic effect of the MWCNTs-CTAB toward the oxidation of Trp.

In addition, the oxidation response of Trp ($30\text{ }\mu\text{mol L}^{-1}$) was followed in phosphate buffer solution ($\text{pH } 3.0$) at the bare GCE and MWCNTs-CTAB/GCE by differential pulse voltammetry (DPV) at a scan rate of 20 mV s^{-1} (Fig. 4). As can be seen, there is only a weak oxidation peak ($I_p \sim 1.59\text{ }\mu\text{A}$) for Trp at the bare GCE. In contrast, at MWCNTs-CTAB/GCE, greatly augmented current response of Trp is obvious. The remarkable peak current enhancement may be attributed to a faster electron transfer rate, higher electrochemical activity, and larger specific surface area of the modified electrode compared to bare GCE.

Effect of pH on the oxidation of Trp

The pH value of electrolyte solution has a significant influence on the oxidations of Trp at the MWCNTs-CTAB/GCE, by varying both the

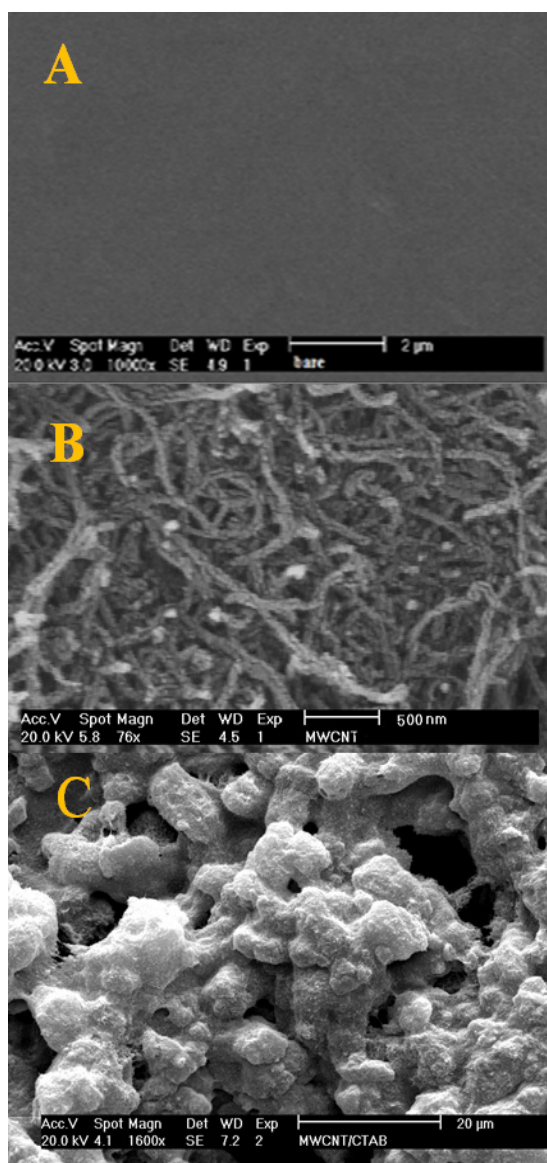


Fig. 1. SEM images of GCE (A), MWCNTs/GCE (B) and MWCNTs-CTAB/GCE (C).

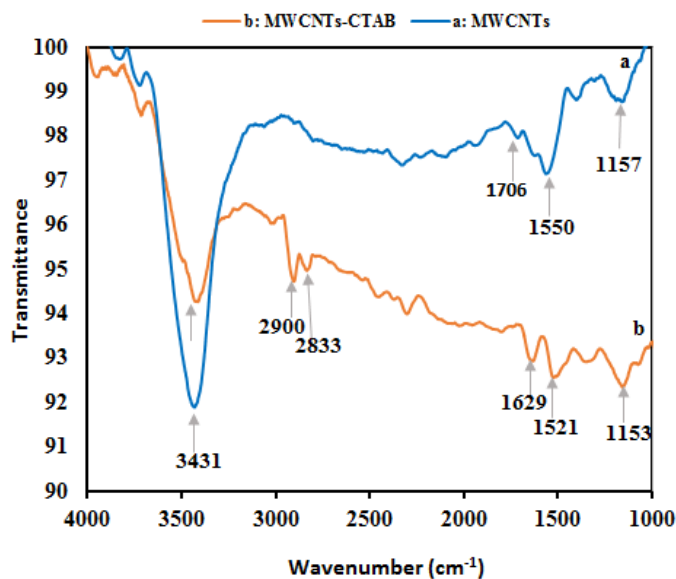


Fig. 2. FT-IR spectra of MWCNTs (curve a), MWCNTs-CTAB (curve b).

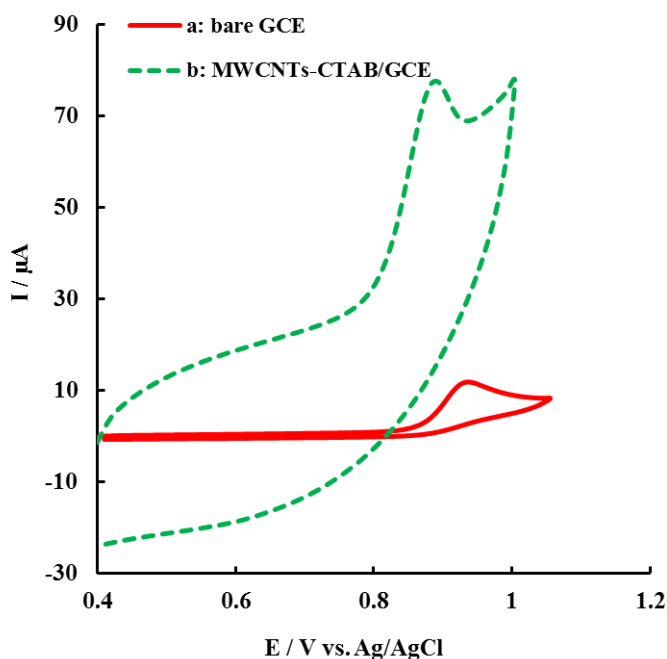


Fig. 3. CV responses of Trp (0.19 mM) on bare GCE (a) and MWCNTs-CTAB/GCE (b) in PBS (pH 3.0); scan rate 100 mV/s.

peak currents and peak potentials. The effect of the electrolyte solution pH value on the peak current and peak potential has been examined by recording the CVs of Trp with the concentrations of $200 \mu\text{mol L}^{-1}$, in a series of phosphate buffer solution of varying pH in the range 2–9. One can see from Fig. 5A that, the peak currents of Trp

increase with the increasing pH value from 2.0 to 3.0 and reach a maximum at pH 3.0, then, they decrease when the pH value increases gradually. In order to get a better sensitivity for sensing Trp, 0.1 M PBS with a pH value of 3.0 has been selected for detecting this species. On the other hand, plot of peak potential against solution pH (Fig. 5B)

showed the shift in oxidation peak potential (E_p) with pH as:

$$E_p \text{ (V)} = 1.0218 - 0.0429 \text{ pH} \text{ (} R^2 = 0.994 \text{)}$$

The slope of 42.9 mV/pH (close to the theoretical value of 59 mV/pH) showed that the uptake of electrons is accompanied by an equal number of protons. This is in agreement with previous works which indicated that two protons and two electrons are involved in the electrochemical process of Trp [5, 15, 17, 20].

Effects of scan rate

Electrochemical mechanisms usually can be acquired from the relationship between peak current and scan rate. The cyclic voltammograms of MWCNTs-CTAB/GCE in phosphate buffer solution at different scan rates were investigated in the range of 20–500 mV s^{-1} . Peak currents of the MWCNTs-CTAB/GCE increased with the increment of the scan rate. A good linear relationship could be observed between the peak current and square root of scan rate in the range of 20–500 mV s^{-1} (Fig. 6A). For 0.24 mmol L^{-1} of Trp, the anodic peak

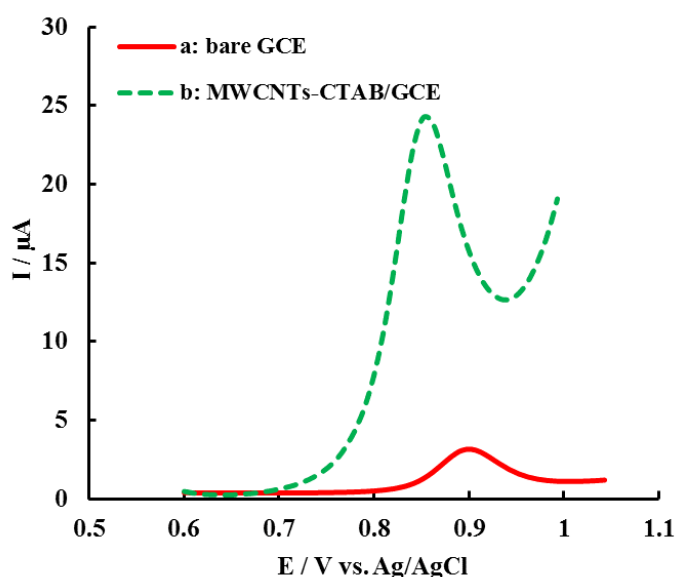


Fig. 4. DPV curves of Trp (30 μM) in PBS (0.1 M, pH 3) on bare GCE (a) and MWCNTs-CTAB/GCE (b).

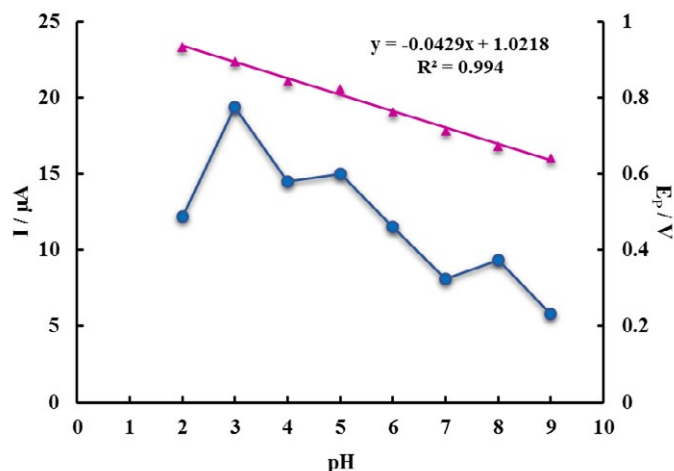


Fig. 5. Plots of peak potential (▲) and peak current (●) against solution pH from cyclic voltammetric study of Trp at MWCNTs-CTAB/GCE.

followed the linear regression equation $I_{pa} (\mu A) = -11.41 + 4.3729 v^{1/2} (mV^{1/2} s^{-1/2})$ ($R^2 = 0.996$), which indicates that the electrode process was controlled by diffusion of Trp to the electrode surface, rather than adsorption (Fig. 6B). In addition, there was a linear relation between $\log(I_p/\mu A)$ and $\log(v/mVs^{-1})$, corresponding to the following equation: $\log(I_p/\mu A) = 0.66291 \log(v/mVs^{-1}) + 0.1645$; $R^2=0.9951$ (Fig. 6C). The slope of 0.66291 was very close to the theoretically expected value of 0.5 for diffusion – controlled processes.

Linear range of Trp detection

Differential pulse voltammetry (DPV), which has a high current sensitivity and a low charging contribution to the background current, was used to construct calibration curve and estimate the lower limits of detection. The DPV curves of solution containing different concentration of Trp showed sharp anodic peaks at ~ 830 mV in PBS (pH 3.0). Fig. 7 displays the DPV curves of different Trp concentrations at the MWCNT-CTAB/GCE. The peak currents increased linearly on increasing the concentration of Trp. The calibration curve for Trp (inset of Fig. 7) represent linear responses in the concentration ranges of 4.9 - 64.1 $\mu mol L^{-1}$

($R^2 > 0.99$). The limit of detection was 1.6 $\mu mol L^{-1}$.

Table 1 presents the comparisons of the linear range and the detection limit results toward Trp determination among MWCNT-CTAB/GCE and the recently reported chemically modified electrodes.

It can be seen, a wider linear dynamic and a lower detection limit in most cases was observed ratio to the proposed method. Whereas, the present sensor is prepared by a simple modification process and the method can be performed using inexpensive equipment in a relatively short time in comparison with other electrodes.

Chronoamperometric measurements

Chronoamperometric measurements of Trp at MWCNTs-CTAB/GCE were carried out by setting the working electrode potential of 900 mV (at first potential step) and 0.0 mV (at second potential step) for various concentrations of Trp. The current is negligible when the potential is stepped down to 0.00 mV, indicating that the oxidation process is irreversible (Fig. 8A). For an electroactive material (Trp in this case) with a diffusion coefficient of D , the current observed for the electrochemical

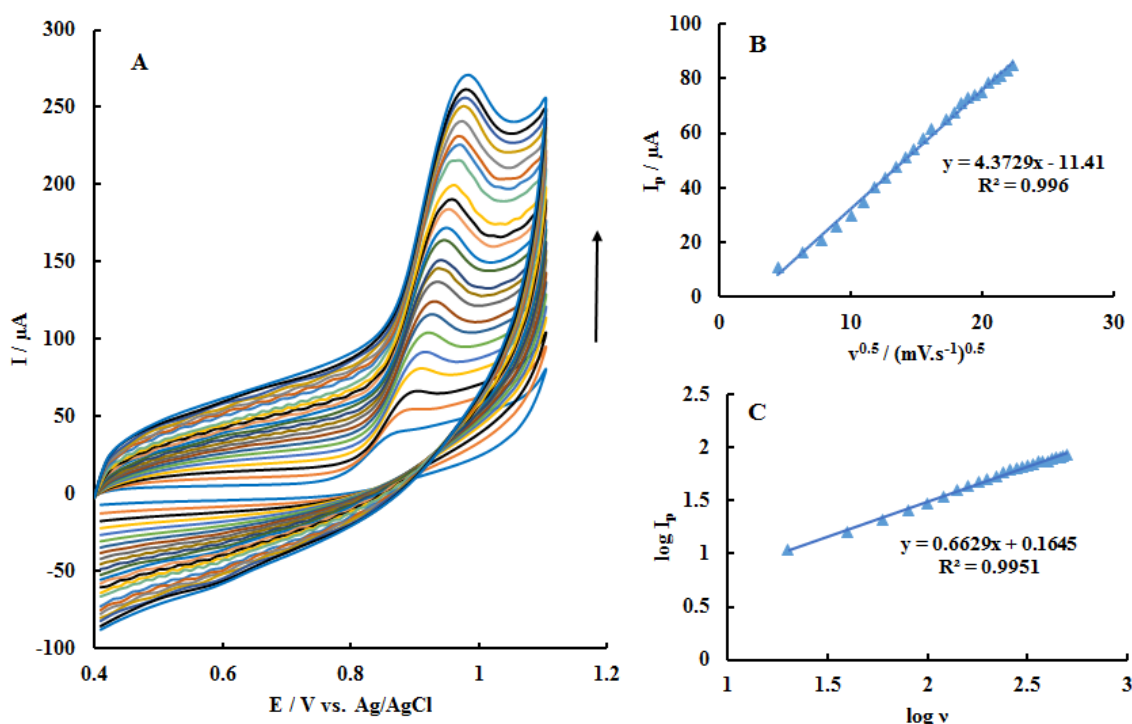


Fig. 6. (A) Effect of scan rate (20-500 $mV s^{-1}$) on the oxidation behavior of Trp in PBS (0.1 M, pH 3.0) at MWCNTs-CTAB/GCE; (B) Linear relationship of I_p against $v^{1/2}$; (C) Log I against $\log v$.

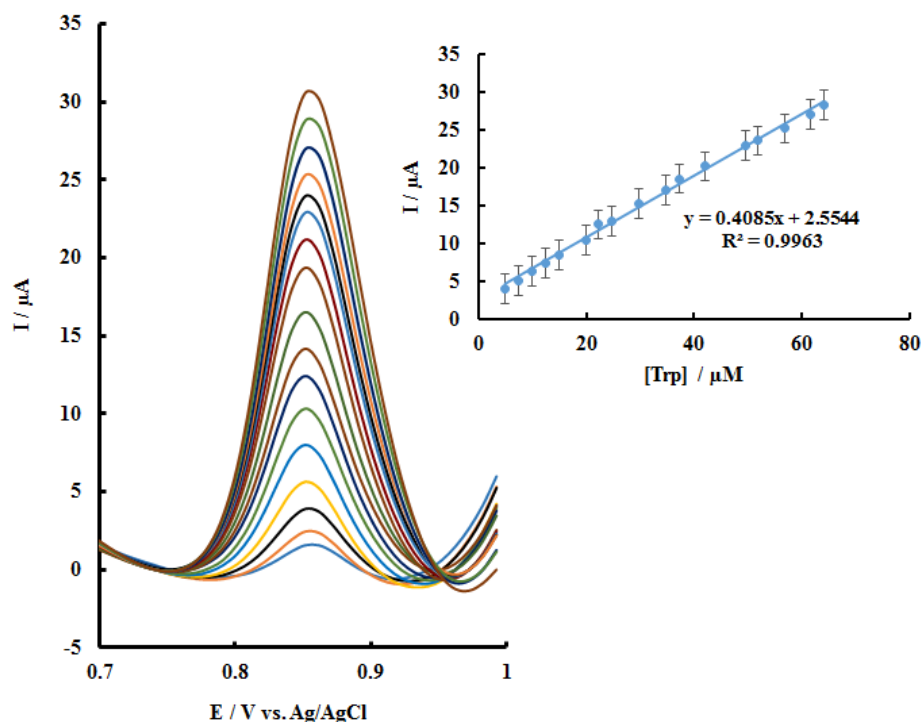


Fig. 7. DPVs at MWCNTs-CTAB modified electrode with varying concentrations of Trp in buffer solution (pH 3.0). Scan rate 20 mV/s, equilibrium time: 5 s. Inset: calibration plot of the dependence of the measured current on Trp concentrations.

Table 1. Comparison of the characteristics of the proposed method with those of previously reported electrochemical methods.

Electrode	Linear range (μM)	Detection limit (μM)	Ref.
MWCNT/cobalt salophen/CNTPE	0.5–50	0.1	[2]
MWCNT/cerium hexacyanoferrate/GCE	0.2–100	0.02	[3]
Nano-TiO ₂ /ferrocene carboxylic acid/ CPE	0.4–14	0.124	[4]
AuNPs/GCE	0.09–50	0.08	[5]
Ni(II)/ACDA/AuNPs/cysteine/gold electrode	0.085–43	0.023	[6]
Pencil graphite electrode	0.5–50	0.05	[7]
4FEPE/CPE	0.85–63.4	0.56	[8]
Poly(9-aminoacridine)/MWCNT/GCE	1–500	0.81	[9]
AuNPs-MWCNT/ITO	0.5–90	0.025	[10]
CuHCF-cysteamine-AuNPs/GW	0.85–120	0.0185	[11]
AuNPs/CILE	5–900	4	[12]
4-aminobenzoic acid/GCE	1–100	0.2	[13]
Copper-cobalt hexacyanoferrate/GE	10–900	6	[14]
Nafion/TiO ₂ -graphene/GCE	5–140	0.7	[15]
AuNPs/CNT/GCE	0.03–2.5	0.01	[16]
Nano-Au/MWCNT/GCE	5–100	3	[17]
Butrylcholine/GCE	2–60	0.6	[18]
Nafion/cucurbit[8]uril/GCE	0.2–4	0.143	[19]
β -Cyclodextrin/Fe ₃ O ₄ /GCE	0.8–300	0.5	[20]
Co ₃ O ₄ /graphene/GCE	0.05–10	0.01	[21]
MWCNTs-CTAB/GCE	4.9–64.1	1.6	This work

reaction at the mass transport limited condition is described by the Cottrell equation. Experimental plots of I vs. $t^{-1/2}$ were employed, with the best fits for different concentrations of Trp. The slopes of the resulting straight lines were then plotted vs. Trp concentration (Fig. 8B). From the resulting slope and Cottrell equation the mean value of the D was found to be $(4.2 \pm 0.1) \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$.

Selective determination of Trp

Selectivity of MWCNTs-CTAB/GCE for the determination of Trp is investigated by adding various possible interferences and observing the change in current. After additions of $50 \mu\text{M}$ Trp, the sensor response is evaluated by the addition of common interfering ions and molecules. Most of the inorganic salts did not interfere in the Trp analysis. Moreover, the results showed that 1000-fold of sucrose, glucose, serine and glycine, 300-fold of L-tyrosine and ascorbic acid, and 6-fold of L-cysteine did not interfere in the determination of Trp. From these results, it may be concluded that the method is free from interference by most foreign substances

Stability, reproducibility and repeatability of MWCNTs-CTAB/GCE

The stability of the modified electrode was tested over a period of one month by storing it in 0.1 mol L^{-1} PBS pH 3.0 at room temperature. No obvious change was observed from the current signal during the first week and decreased about 3.42% of its initial responses for $30 \mu\text{mol L}^{-1}$ Trp after another 3 weeks, indicating the good stability of the modified electrode.

For six successive measurements of Trp ($30 \mu\text{mol L}^{-1}$), a relative standard deviation (R.S.D.%) of 3.57% was calculated, suggested good repeatability of the method. In order to study the reproducibility of the new sensor for Trp analysis, six modified electrodes were fabricated independently and were used to determine Trp ($30 \mu\text{mol L}^{-1}$). R.S.D.% was 3.35%, revealing an excellent reproducibility of the electrode preparation procedure.

Real sample analysis

To demonstrate the suitability and potential application of MWCNTs-CTAB/GCE for Trp analysis in complex real samples, the proposed method

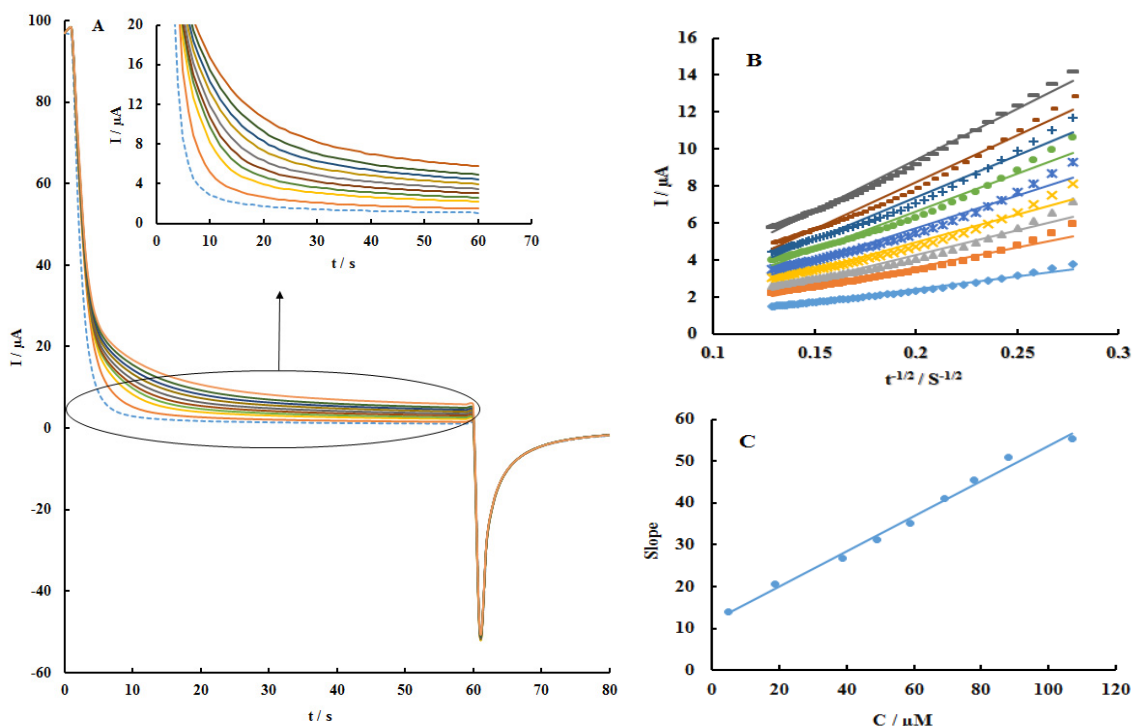


Fig. 8. (A) Chronoamperograms of MWCNTs-CTAB/GCE in 0.1 M phosphate buffer (pH 3.0) containing different concentrations of hydrazine; chronoamperograms correspond to 0.0, 4.9, 19, 39, 49, 59, 69, 78, 88 and $107 \mu\text{M}$ of Trp (from bottom to top). (B) Plot of I versus $t^{-1/2}$ from the data of chronoamperograms for different concentrations of Trp. (C) The slopes of resulting straight lines from (B) versus Trp concentration; potential steps = 0.9 and 0.0 V.

Table 2. Results of recovery test of Trp in human serum samples (n = 3).

No.	Added (μM)	Found (μM)	Recovery (%)
1	0	Not detected	
2	9.98	9.39	94.1
3	19.92	19.4	97.45
4	29.82	31.03	104.08
5	39.68	41.16	103.7
6	49.5	47.92	97.0

was applied to the determination of Trp in spiked human blood serum samples. The contents were determined using the standard addition method (Table 2). Five replicate determinations were performed and satisfactory results were obtained. The percentage recovery was 94.1 – 104.08% confirming the independence of the method from the matrix interference. RSD% values were in the range of 2.2 - 4.2% which shows the precision of successive determinations.

CONCLUSION

In summary, a simple strategy for detection of Trp at MWCNTs-CTAB/GCE electrode was presented in this paper. The experimental results demonstrated that the MWCNTs-CTAB/GCE electrode exhibited excellent electrocatalytic activity towards the oxidation of Trp with obvious increase in peak current. In DPV mode and under optimized experimental condition, the linear range 4.9 - 64.1 $\mu\text{mol L}^{-1}$ and limit of detection of 1.6 $\mu\text{mol L}^{-1}$ can reach. Determination of Trp in human blood serum was carried out by using the modified electrode in DPV regime. The calculated recoveries were 94.1 -104.08% for micromolar concentrations of tryptophan. The modified electrode had a good stability and reproducibility. Furthermore, the modified electrode has a long lifetime.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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