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Full Paper

Voltammetric Determination of Methadone at Stacked Cysteic Acid Film and Gold Nanoparticles Composite Modified Glassy Carbon Electrode

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Abstract- In this paper, a sensitive and convenient electrochemical sensor based on stacked cysteic acid film and gold nanoparticles (AuNPs) composite modified glassy carbon electrode (GCE) was developed for the determination of Methadone (MET). Electrochemical investigation of the modified electrode is achieved using cyclic voltammetry (CV), differential pulse voltammograms (DPV) and field emission scanning electron microscopy. The effective surface areas of AuNPs/cysteic acid/GCE increased for about 4-fold larger than that of the unmodified GCE. The kinetic parameters of the electron transfer coefficient (α) and number of electrons involved in the rate determining step (n_α) for the oxidation of MET were determined utilizing CV. The designed modified electrode was revealed linear responses in the ranges of 0.024 to 4.45 μM and 4.45 to 12.67 μM with a limit of detection (LOD) of 0.014 μM (S/N=3). Excellent recovery results were obtained for determination of MET in spiked human blood plasma and urine samples at the modified electrode.

Keywords- Methadone, Gold nanoparticles, Cysteic acid, Electrochemical sensor, Modified electrode

1. INTRODUCTION

Methadone (6-dimethylamino-4, 4-diphenyl-3-heptanone or Dolophine, MET), is a synthetic analgesic drug, which has been widely used for the treatment of opioid dependence

since the mid-1960s [1,2]. The treatment has been controversial as it replaces a short-acting opioid (heroin) with a long-acting one [3,4]. The mechanism of action by which MET can alleviate opioid dependence and diminishing symptoms in affected individuals, have been discussed thoroughly [5]. Overdose symptoms MET include, Psychological: Drowsiness, sedation, dizziness, lightheadedness, mood swings (euphoria to dysphoria), depressed reflexes, altered sensory perception, stupor, coma and Physiological: Strong analgesia, headache, dry mouth, facial flushing, nausea, constipation, respiratory depression, muscle flaccidity, pupil constriction, and decreased heart rate [6-8]. Accordingly, accurate analytical method for MET is necessary.

In view of the prominence of MET in clinical applications, various efforts have been made for the determination of MET, including high performance liquid chromatography (HPLC) [9, 10], capillary electrophoresis [11], liquid chromatography [12,13], atomic absorption and atomic emission spectrometry [14] gas chromatography [15-17], liquid chromatography tandem mass spectrometry (LC-MS/MS) [18] and electrochemical techniques [19-22]. These methods suffer from some disadvantages such as high cost, long analysis time and requires more complex, tedious sample pretreatment. In some cases, low sensitivity and selectivity makes them unsuitable for a routine analysis. It is essential to look for a new method with high sensitivity, simplicity and efficiency for the detection of this drug. Among the various quantification techniques, electrochemical methods found to be effective for the determination of several pharmaceutical compounds as they are faster, cost effective, easier and sensitive than spectrophotometric, HPLC and other reported methods. Moreover, electrochemical techniques are successfully applied for the determination of the drug substance in the complicated systems like tablets and biological fluids. Therefore, different electrochemical techniques based on various chemically modified electrodes have been widely explored for the determination of MET [19-23].

In the last decade, electrochemical sensors with nanoparticles have received enormous attention owing to their high surface area and unique electrochemical properties [24-26]. The use of nanomaterials greatly improved the sensitivity and stability of those sensors [27-29]. As the most stable noble metal nanoparticles, Au nanoparticles (AuNPs) can enhance electrode conductivity, facilitating the electron transfer, high effective surface area, control over surrounding environment and improving the detection limit for biomolecules [30-33]. To utilize AuNPs for the fabrication of novel electrochemical sensors, they must be attached to electrode substrates. Generally, self-assembly technology [34], electrochemical deposition [35] and seed mediated growth method [36] are widely used. Moreover, the porous structure of conducting polymer allows dispersing of the metal nanoparticles into the polymer matrix and generates additional electrocatalytic sites [37,38]. L-Cysteine is an important amino acid owing to its crucial roles in biological systems. Because of having sulfhydryl, L-cysteine

could be electrochemically oxidized to cysteic acid, which forms a novel thin film material at surface of electrode.

In the present work we describe the development of a AuNPs/cysteic acid modified GCE that offers substantial improvements in the kinetics and sensitivity of the voltammetric responses toward MET. The AuNPs/cysteic acid coated GCE described in the present work, offers marked acceleration of the MET electrooxidation compared to the individual (cysteic acid) modified electrodes. These behaviors, along with detailed characterization of the AuNPs/cysteic acid modified electrode are reported in the following sections.

2. EXPERIMENTAL

2.1. Chemicals and Solutions

All chemicals were commercially available and were used as received. Hydrogen tetrachloroaurate ($HAuCl_4$), Methadone (MET), were from Sigma–Aldrich. L-Cysteine, Methanol and NaH_2PO_4, Na_2HPO_4 were obtained from Merck, Stock solutions of MET (1mM) were prepared in water and kept in the dark in refrigerator. Cysteic acid stock solution was prepared daily by dissolving in 0.1 M Phosphate buffered solutions (PBS), (pH 7.0) as required. Doubly distilled water was used throughout the work.

2.2. Apparatus

Electrochemical experiments were performed using an Autolab (Eco Chemie B.V., Ultrecht, the Nether-lands) controlled by the GPES software (Version 4.9). A conventional three-electrode cell was used with a saturated Ag/AgCl as reference electrode, a Pt wire as counter electrode and a GCE or modified GCE as working electrode. The pH values were measured with a Metrohm pH-meter (Model: 691Herisau, Switzerland), supplied with a glass-combined electrode. The general morphology of the products was characterized by field emission scanning electron microscopy (FESEM Mira 3- XMU).

2.3. Fabrication of AuNPs/cysteic acid modified glassy carbon electrode

Before modification, the surface of GCE was polished by 0.05 μm alumina in a water surrey using a polishing cloth, and then sonicated in distilled water for 5 minutes. Cysteic acid/GCE was prepared by electrochemical oxidation of L-cysteine through dipped GCE in 0.1 M PBS (pH 7.0) containing 10 mM L-cysteine in the potential range of −0.8 to 2.2 V at 100 mV s^{-1} for 15 cycles [39,40]. Finally, to construct the AuNPs modified cysteic acid/GCE was immersed into 1 mM hydrogen-tetra-chloroaurate $HAuCl_4$ solution containing 0.1 M KCl solution as electrolyte, and electrochemical deposition of Au nanoparticle was conducted at -0.4 V versus Ag/AgCl was applied for 100 s [40,41]. Then, the modified

electrode was washed with doubly distilled water and dried carefully. The obtained electrode was denoted as AuNPs/cysteic acid/GCE.

2.4. Analysis of Spiked Human serum and urine

Healthy blood serum samples were obtained from the laboratory of pastor (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.

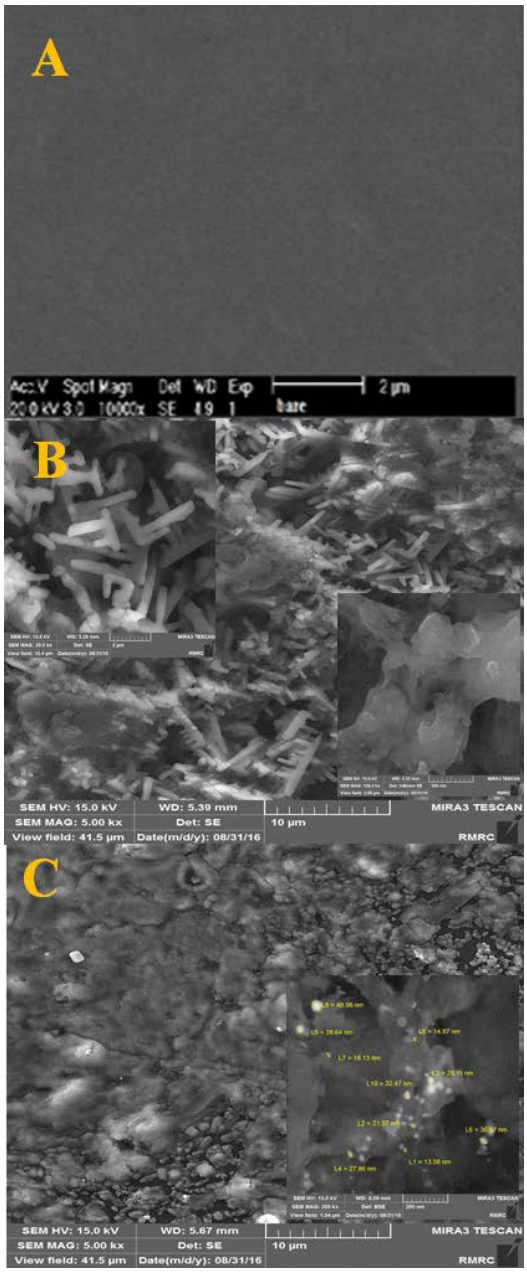


Fig. 1. FESEM images of unmodified GCE (A), Cysteic acid/GCE (B) and AuNPs/Cysteic acid/GCE (C)

After 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 M, pH 7.0). The standard addition method was used for the determination of MET in serum samples.

The human urine samples were spiked of with 4.9 µM MET treated in 0.2 mL of methanol for subsequent removal of the proteins. These samples were agitated and placed in a micro centrifuge during 3 min at 5000 rpm. The superior liquid was removed and transferred to a solution of 10 mL of PBS pH 7.

3. RESULTS AND DISCUSSION

3.1. Morphologies of the different electrodes

The response of an electrochemical sensor was related to its physical morphology. The surface morphology of the unmodified GCE and modified electrodes were characterized by Field emission scanning electron microscopy (FESEM). Comparison of FESEMs of unmodified GCE (Fig. 1A) with Cysteic acid/GCE (Fig. 1B) shows Cysteic acid was assembled on the GCE surface as citrate like structure. The whole assembly on electrode surface (AuNPs/Cysteic acid/GCE) is shown in image Fig. 1C, in which the Au nanoparticles are observable. Statistical analysis of SEM data showed that the average diameter of AuNPs was 20±5 nm.

3.2. Electrochemical behavior of MET at the surface of various electrodes

The electrochemical behavior of MET in phosphate buffer solution (pH=7) was investigated at the surface of GC, Cysteic acid/GC, AuNPs/Cysteic acid/GC elecrodes and the results are presented in Fig. 2. As it is seen an anodic peak with different intensities without any counterpart cathodic peak at the reversed scan is observed on all tested electrodes for MET over the potential range of 0.4–1.0 V (curves a–c), revealing the irreversible nature of the oxidation process of MET at different modified electrodes. The lowest peak current appeared on the unmodified GCE (curve a). The anodic peak potential at a Cysteic acid/GCE under identical conditions is about +0.81 V (curves b) so, a decrease in overpotential is observed, and in comparison with unmodified GCE the peak current was increased significantly at Cysteic acid. After modification of the Cysteic acid/GCE with AuNPs, the electrode sensitivity was further improved and its resistance to MET oxidation was reduced which could be attributed to the high conductivity and large specific surface area of the AuNPs (curves c).

The differential pulse voltammograms for 4.9 µM MET at the unmodified GCE (a), Cysteic acid/GCE (b) and AuNPs/Cysteic acid/GCE (c) are shown in Fig. 3. The oxidation

peak of MET appeared on unmodified GCE, Cysteic acid/GCE (b) and AuNPs/Cysteic acid/GCE at about 800.6 mV, 750.3 mV, 761.8 mV, respectively.

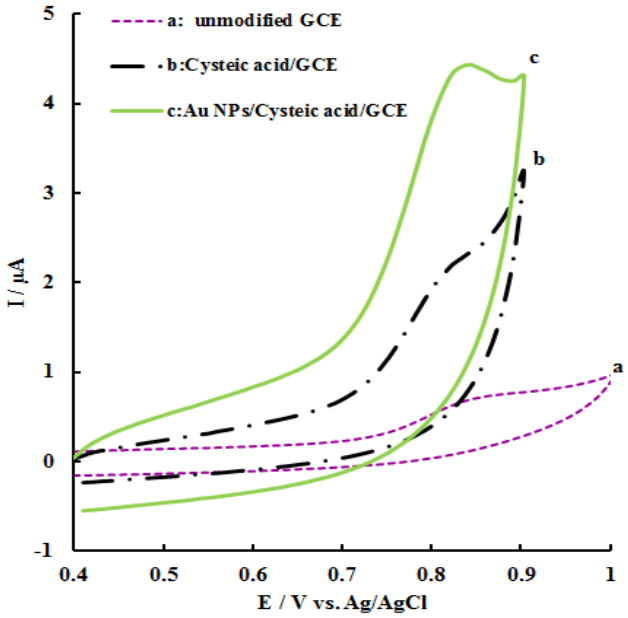


Fig. 2. Cyclic voltammograms of 4.9 µM MET in 0.1 M PBS (pH 7.0) at the surface of different electrodes: unmodified GCE (a), Cysteic acid/GCE (b) and AuNPs/Cysteic acid/GCE (c) at scan rate of 100 mV s^{-1}

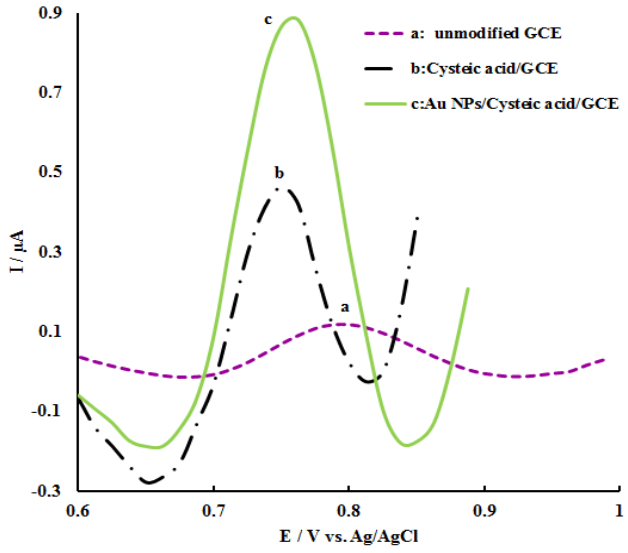


Fig. 3. Differential pulse voltammogram of 4.9 µM MET on unmodified GCE (a), Cysteic acid/GCE (b) and AuNPs/Cysteic acid/GCE (c) in pH 7.0 phosphate buffer solution at Scan rate 20 mV s^{-1} and pulse amplitude 50 mV

As can be seen from the voltammograms, a rather low oxidation signal of MET was obtained on unmodified GCE. Also, based on the voltammograms, Cysteic acid increased the surface of the electrode individually, which led to a signal enhancement for MET electrode's, while in AuNPs/Cysteic acid/GCE the electrode signal enhancement is more than the two other electrodes. The results indicate that AuNPs/Cysteic acid hybrid exhibit remarkable ability to increase the electroactive surface area and enhance the electron-transfer between the electrode and the analyte.

3.3. Optimization of variables

3.3.1. Influence of pH

Cyclic voltammetry was carried out to characterize the effects of solution pH on oxidation peak potential of MET at the AuNPs/Cysteic acid nanocomposite modified GCE. Fig. 4 presents the effect of pH value on the peak current and peak potential for 5.96 µM MET in various pH values of PBS. The results showed that the E_{pa} shifted to lower values as the pH increased.

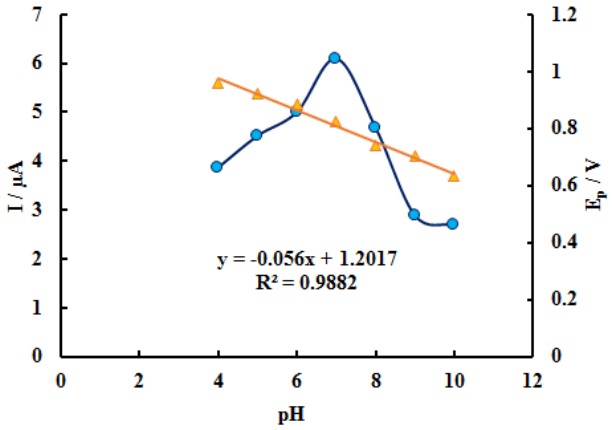
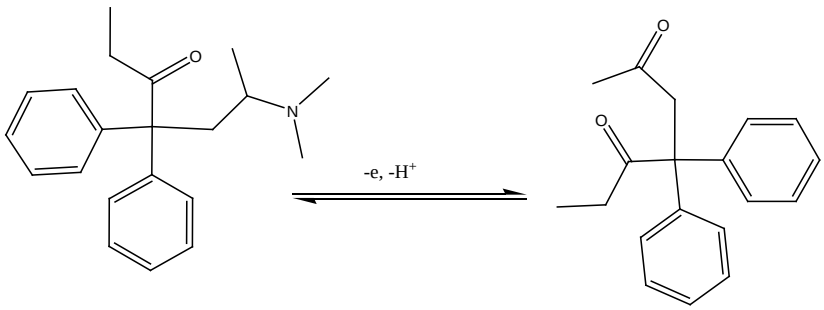


Fig. 4. Dependence of anodic peak potential (▲) and anodic peak current (●) as a function of solution pH



Scheme 1. The electrochemical oxidation mechanism of methadone

The relationship between the E_{pa} and pH could be fitted into the regression equation: E_{pa}(V)=1.2017-0.056 pH (R=0.9882), whose slope indicates that the same amounts of electrons and protons took part in the electrode reaction [20,21], which is consistent with the previously reported mechanism (Scheme 1). In addition, the maximum current responses of MET were obtained at pH 7.0. Therefore, pH 7.0 was chosen for the subsequent analytical experiments.

3.3.2. Effect of electro-polymerization cycles

In order to study the influence of the number of cycles applied during the electropolymerization on response characteristics several sensors were fabricated in a 0.1 M PBS aqueous buffer pH 7.0 containing 10 mM L–cysteine, to cover the range between 5 and 25 cycles.

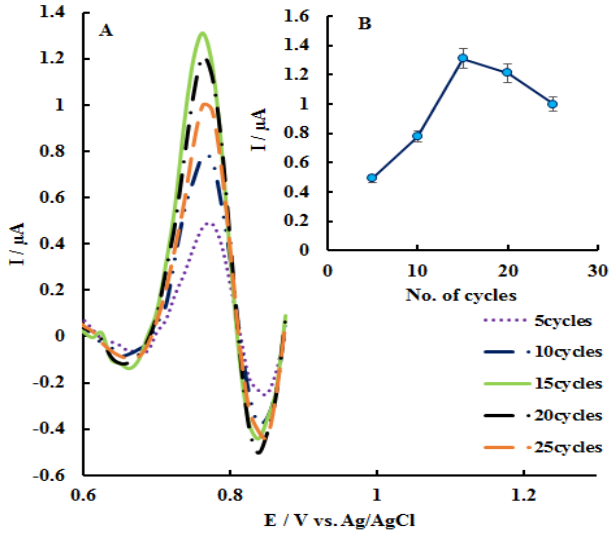


Fig. 5. Differential pulse voltammograms of 5.9 µM MET on the surface of AuNPs/cysteic acid/GCE with various numbers of polymerization cycles; (B) corresponding curve of peak current versus number of polymerization cycles

The sensors were checked for amounts of MET, as can be seen in Fig. 5, the greatest current was observed for a film prepared with 15 cycles. An increase in response was observed up to 15 cycles, followed by a subsequent decrease in response corresponding for higher cycles. Consequently L –cysteine number of 15 cycles was chosen as the optimum and was used in all subsequent analyses with which it was possible to obtain higher and more reproducible signals.

3.3.3. Effect of potential scan rate

Sweep rate studies were performed in the range 10-120 mV s^{-1} (Fig. 6A). The analyte peak current was found to increase with increasing sweep rate. Scan rate studies were carried out to assess whether the processes on AuNPs/cysteic acid/GCE were under diffusion or adsorption control.

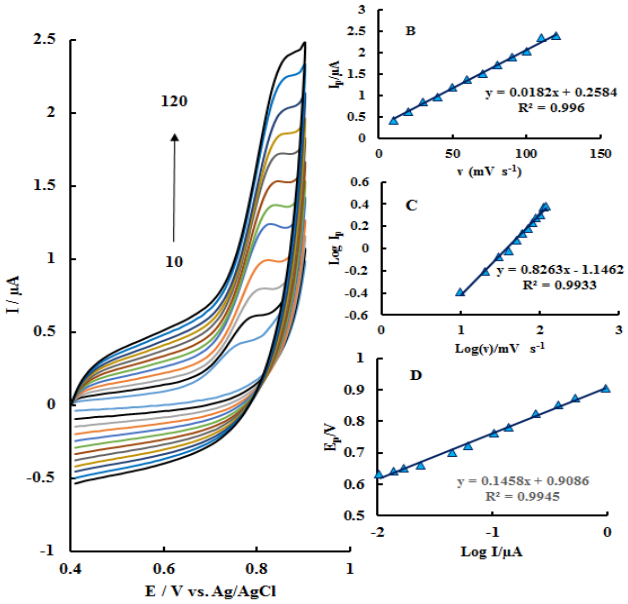


Fig. 6. (A) Cyclic voltammograms of 3.96 µM MET on the AuNPs/cysteic acid/GCE at different scan rates (10-120 mV s^{-1}) in PBS (pH 7.0). (B) The plot of the peak current versus scan rate. (C) Plot of logarithm of peak current versus logarithm of scan rate and (D) Tafel plot derived from the rising part of voltammogram recorded at a scan rate 5 mV s^{-1}

A good linearity was obtained between oxidation peak current and scan rates (Fig. 6B). The result indicates that the electrode process is controlled by the adsorption of MET. A plot of logarithm of peak currents versus logarithm of scan rates (Fig. 6C) give a straight line with slope of 0.8263, which is toward the theoretical value of 1.0, and it is expected for an ideal reaction with the adsorption-controlled electrode process [42-44].

In order to obtain more information about the rate-determining step, the Tafel plot (plot of E *vs.* log I) was drawn for AuNPs/cysteic acid/GCE in the presence of 3.96 µM MET (Fig. 6D). The results showed an average Tafel slope of 0.1458 $decade^{-1}$ with R^2=0.9945. The slope of the Tafel plot was equal to 2.3RT/n (1−α) F. Thus, we obtained a value for equal to 0.41, which confirms the symmetry of the voltammograms.

3.3.4. Effect of Accumulation Time

It was significant to fix the accumulation time when adsorption studies were intended. The effect of accumulation time for 2.97 μM MET was investigated ranging from 10 to 60 s. As shown in Fig. 7, the peak current increased gradually as the accumulation time increased from 10 to 30 s. However, with further increasing in accumulation time beyond 30 s, the peak current decreased and tended to be almost stable. Therefore, the optimal accumulation time of 30 s was chosen in further investigates.

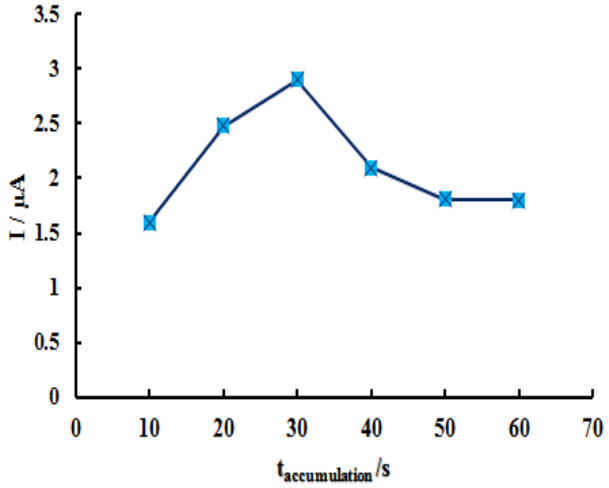


Fig. 7. Effect of accumulation time of 2.97 μM MET at AuNPs/cysteic acid/GCE

3.4. Calibration graph

In order to test the feasibility of the exploited method for the determination of MET, the relationship between the anodic peak current and the concentration of MET was studied using differential pulse voltammetry under the optimum conditions (Fig. 8). The plot of peak current *vs.* MET concentration consisted of two linear segments with slopes of 0.1741 and 0.1023 μA μM^{-1} in the concentration ranges of 0.024 to 4.45 μM and 4.45 to 12.67 μM, respectively. The difference in the slopes for the calibration curves is due to the different activity of the electrode surface with low and high concentrations of the analyte. In the lower MET concentration, due to a high number of active sites (in relation to the total number of the analyte molecules), the slope of the first calibration curve is high. While in the higher MET concentration, due to decreasing active sites (in relation to the total number of analyte molecules, mainly at the surface of the electrode), the slope of the second calibration decreased too.

Also, The limit of detection defined as $LOD=3S_b/m$, where LOD, S_b and m are the limit of detection, standard deviation of the blank and the slope of the calibration graph, respectively, was found to be 0.014 μM. Detection limit and linear calibration range of the

proposed method were compared with those of other reports and the results are summarized in Table 1. As can be seen, detection limit and linear range are comparable or better than the other MET sensors.

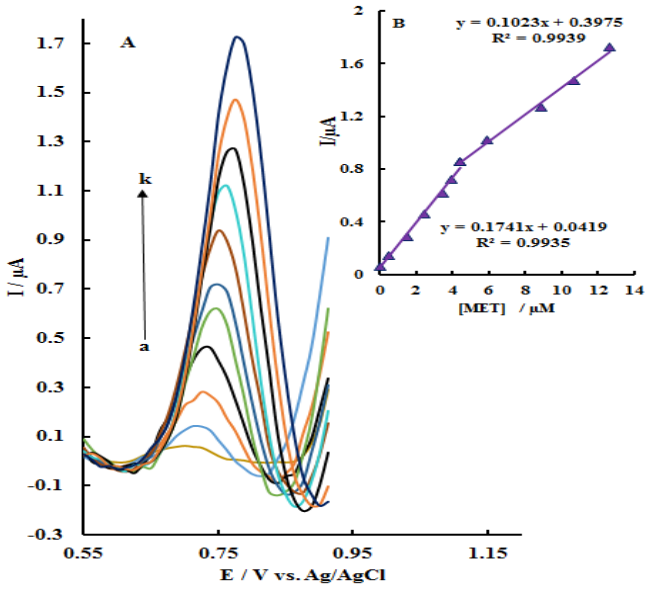


Fig. 8. (A) Voltammograms and (B) respective calibration curve for increasing concentrations of MET, from (a-k) 0.024 to 4.45 µM and 4.45 to 12.67 µM in PBS 0.1 M under the DPV optimized conditions at AuNPs/cysteic acid/GCE

Table 1. Comparison of major characteristics of different materials electrochemical sensors for determination MET

Electrode	Linear range (µM)	LOD (µM)	Ref.
MWCNT/GCE	0.5–100	0.28	[21]
GNPs/MWCPE	0.5-300	0.005	[19]
CPE	1-10	0.97	[23]
MWCNT-PGE	0.1-15	0.087	[20]
Au NPs /Cysteic acid /GCE	0.02-4.45; 4.45-12.67	0.014	This Work

3.5. Electrochemical sensor reproducibility and stability

Under the optimized conditions, the AuNPs/cysteic acid/GCE was used to determine 2.97 µM MET by DPV. The relative standard deviation (RSD) was 3.6%, which indicates that the electrochemical response of MET at the AuNPs/cysteic acid/GCE was highly reproducible.

Five different AuNPs/cysteic acid/GCE were fabricated and the RSD for the detection of 2.97 μM MET is 2.19%, revealing excellent repeatability of AuNPs/cysteic acid/GCE. When the electrode was kept at 4 ˚C in a refrigerator for two weeks, the oxidation peak current of MET only decreased 3.4%, suggesting good stability.

3.6. Interferences

To study the effect of presence of other species on the oxidation of MET, oxidation peaks were recorded at AuNPs/cysteic acid/GCE in 2.97 μM MET solutions (pH=7.0) and in same solutions which contained foreign species. Then the oxidation currents were compared together. The tolerance limit was taken as the maximum concentration of foreign species which caused no more than ±5% relative error in the oxidation current. Several metabolites present in urine or blood may alter the electrochemical signal of the sensor and consequently affect the selectivity of developed method. Ascorbic acid (AA), epinephrine (EP), acetaminophen (ACT) and tryptophan (Trp) are common metabolites present in biological systems, which can interfere in the electrochemical response of MET. It was found that at the AuNPs/Cysteic acid/GCE, the oxidation peaks of ascorbic acid AA, epinephrine EP, acetaminophen ACT and tryptophan Trp were observed at -0.01, 0.15, 0.338, 0.62 V, respectively (Fig. 9).

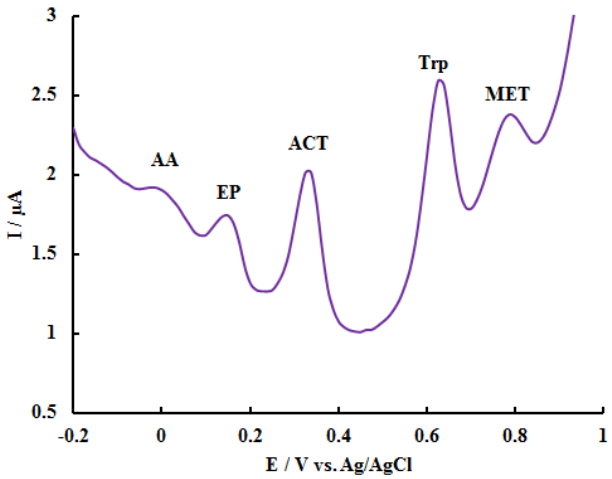


Fig. 9. DPV of MET **(**2.97 μM) in the presence of ascorbic acid (AA), epinephrine (EP), acetaminophen (ACT) and tryptophan (Trp)

It was found that there was no significant change in the anodic peak current response of MET up to 100-fold excess of each of the interferents. It demonstrated that the AuNPs/Cysteic acid/GCE exhibited excellent selectivity for detection of MET without interference of other coexisting species.

3.7. Analytical applications

In order to examine the reliability and feasibility of the proposed modified electrode for practical analyses, recovery experiments were performed by standard addition methods in spiked blood serum and urine as the real sample. The experimental results are listed in Table 2. They show an acceptable recovery. These results also indicate that the proposed AuNPs/cysteic acid/GCE might provide a feasible alternative tool for the detection of MET in human serum and urine samples for routine clinical diagnosis.

Table 2. Results of recovery tests for determination of MET spiked in human blood plasma and urine samples by DPV technique using Au NPs /cysteic acid /GCE

urine sample	**added[µM]**	**founded[µM]**	**Recovery%**
1		No detected	
2	1.99	1.98	99.4
3	3.98	3.93	98.8
4	7.93	7.83	98.7
5	9.9	10.2	103
Human blood serum	**added[µM]**	**founded[µM]**	Recovery%
1		No detected	
2	0.99	1.01	102
3	1.99	1.97	98.9
4	2.99	2.95	98.6
5	3.98	4.02	100.7

4. CONCLUSIONS

Electrochemical behavior and determination of MET was investigated on the Au NPs /cysteic acid /GCE. The electro-oxidation mechanism of MET at the fabricated electrode was an adsorption controlled irreversible process involving one-electrons and one-protons. The DPV signal of MET increased linearly over the concentration range 0.024 to 4.45 µM and 4.45 to 12.67 µM with a detection limit of 0.014 µM. The proposed sensor was applied for the determination of MET in human blood plasma and urine samples with satisfactory results making it practical for routine analysis.

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