Carbon Paste Electrode with Au/Pd/MWCNT Nanocomposite for Nanomolar Determination of Timolol

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Fabrication of Au/Pd/MWCNT nanocomposite was performed by using chemical method. The nanocomposite was characterized by scanning electron microscopy (SEM), energy-dispersive X-Ray spectroscopy (EDS) and electrochemical methods. Palladium and gold nanoparticles were dispersed in multi-walled carbon nanotubes (MWCNT). The Au/Pd/MWCNT nanocomposite was applied as a modifier in carbon paste electrode for electro-oxidation of timolol. This modified electrode displayed high efficiency for sub-micromolar determination of timolol maleate. The effect of pH of the buffered solutions and potential sweep rate on the response of the electrode for the oxidation of timolol were investigated. Differential pulse voltammetry was used for quantitative determination. Dynamic linear ranges were obtained in the two ranges of 1.0×10^{-5} - 1.0×10^{-3} M and 5.0×10^{-9}- 8.0×10^{-7} M and the detection limit was estimated to be 5.8×10^{-11} M. The practical utility of this modified electrode was investigated by detecting timolol maleate in pharmaceutical sample (eye drop) and synthetic serum.

1. INTRODUCTION

Timolol maleate (TM), (S)-1-[(1, 1-dimethyl) amino]-3[4-(-morpholinyl9-1, 2, 5-thiadiazol-3-yl) oxy]-2-propanol is a non-specific beta-adrenergic blocking drug which applied to treat high blood pressure, angina (heart pain), heart attacks and migraine headaches [1]. TM (scheme. 1, TM) was the first β-blocker that has been used as an antglaucoma agent. Investigating TM concentrations in ophthalmologic solutions, tablets and urine is an important issue which required sensitive methods. In recent literature, various analytical techniques have been applied for detection of TM such as liquid

chromatography [3, 4], high performance liquid chromatography [5], high performance thin layer chromatography [6], and spectroscopic methods [7-10]. However, most of these methods are time consuming, reagent consuming, expensive and need skillful operators. Compare to these techniques, electrochemical methods are cheaper, simpler and faster [11-14]. A few electrochemical methods for determination of TM have been reported [2, 11- 14] which most of them are based on reduction of TM. Unfortunately, some of these methods used the toxic and expensive mercury electrodes for TM detection [12, 13]. Carbon paste electrodes (CPEs) have been applied as an adaptable working electrode. Easy modifiability of CPEs, which improve electrode efficiently, made them efficient working electrodes for detecting various analytes [15].

Carbon nanotubes (CNTs), due to their outstanding mechanical, electrical, chemical properties, thermal stability and high aspect ratio have been applied in sensors [16, 17]. The CNTs material have other benefits over supporting material such as having more defined crystalline structure with high conductivity, eliminating potential poisoning effects to electrocatalysts due to containing little impurities and having three dimensional structure thus favoring the flow of reactant and preparing a large reaction zone when applied into electrodes [18]. Multi-walled carbon nanotubes (MWCNT) can be used as highly conducting support dispersion of metal nanoparticles due to their large surface area and morphology [19, 20]. In addition, MWCNT can be applied to improve electron transfer reactions. The decoration of MWCNTs with metal NPs has been introduced in new fields of possible applications especially as modifier in CPEs [18-22].

Metal nanoparticles (NPs) have been attracted lots of interest due to their unique physical, optical, electronic, catalytic and magnetic properties [13, 14, 23, 24]. NPs improve the redox process significantly, which is the reason of their vast applications at sensors and biosensors [23, 24]. Among the metal NPs, gold and palladium NPs have been applied widely in various field of technology [24-32].

AuNPs have a vast application in the field of electronics, catalysis and biosensors and due to their large aspect ratio; biocompatibility and high electrical conductivity have been widely employed as modifiers [24, 25]. On the other hand, palladium is an important noble metal NP due to its better stability and well understood physicochemical properties [26] and it has been applied widely in catalytic applications including hydrogenations [27, 28] oxidations [29, 30] and electrochemical reactions [31, 32]. Gold and palladium NPs mixture shows an interestingly high activity toward useful chemical reaction [33-37]. Catalytic activity of metal NPs can be significantly affected by the applied substrate [38-42].

In this work, Au/Pd/MWCNT nanocomposite has been prepared and characterized. By profiting from excellent electrocatalytic properties of combination of MWCNT and Au/Pd NPs, an efficient modifier was prepared to fabricate a modified CPE to detect and study electrocatalytic oxidation of TM in real samples.
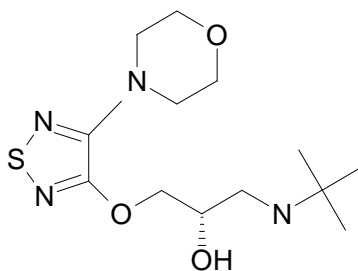
Scheme 1. The structure of TM.

2. EXPERIMENTAL

2.1 Chemicals and reagents

Multi-walled carbon nanotube synthesized by catalytic chemical vapor deposition (CVD, purity N 95%) with outer diameter (o.d.) of 10 – 20 nm, inner diameter (i.d.) of 5 –10 nm and tube length of 0.5 –200 nm was obtained from Nanostructured & Amorphous Materials (Houston, TX, USA), H_2PdCl_4 and $HAuCl_4$, were purchased from Sigma Aldrich, timolol (purity >99.5%) was provided from U.S. Pharmacopeial Convention (USP). All other chemical were analytical reagent grade from Merck. All aqueous solutions were prepared with doubly distilled deionized water. Britton–Robinson (B–R) (0.04 M) buffer solutions of pH 2.0–9.0 (CH_3COOH + H_3BO_3 + H_3PO_4) were used as the supporting electrolyte. The pH was adjusted using 0.2 M NaOH. Voltammetric experiments were carried out in the buffered solutions, which were deoxygenated by purging the pure nitrogen. Deionized and ultra-pure water were taken from a Millipore water purification system.

2.2 Apparatus

All Voltammetric experiments were performed using potentiostate/galvanostate Autolab model PGSTAT12/30/302. A conventional three-electrode system was used for all electrochemical experiments with a CPE as working electrode, a KCl-saturated calomel reference electrode (SCE) and a platinum wire as the counter electrode. A digital pH/mV/Ion meter (Inolab WTW series) was employed for preparing buffer solutions. The scanning electron microscope (SEM) images were obtained applying Hitachi S-4800 Ultra-High Resolution coupled with energy dispersive X-ray spectroscopy (EDS) (S4800).

2.3 Procedure I: Multi-walled carbon nanotube materials pretreatment

Different purification methods have been applied to remove the probable amorphous carbons and metallic impurities, and to improve the electron transfer properties and allow further functionalization [43]. According to one of the suggested methods in literature, 500 mg of the prepared

MWCNT was heated in an oven at 400 °C in nitrogen atmosphere for 2 h. To eliminate metal oxide catalysts, the heated processed amount MWCNT was dispersed in 50 mL of 6.0 M HCl for 2 h under ultrasonic agitation and under the nitrogen atmosphere then filtered on a Watman 42 filter paper and washed with doubled distilled water until the pH of the solution became neutral; and finally, dried [44].

2.4 Procedure II: Preparation of Au/Pd/MWCNT nanocomposite

Pd/MWCNT nanocomposite and Au/Pd/MWCNT nanocomposite were synthesized chemically with a same way by using literature methods [47, 48]. 20 mg of treated MWCNT was dispersed in 20 mL ethanol/water (1:1, v/v ratio) in a beaker to form a uniform suspension for 5 min. Then the suspension was mixed with 10 mL of 5.0×10^{-3} M of H_2PdCl_4 and 5.0×10^{-3} M of $HAuCl_4$ and stirred for 12 h. A fresh 50 mg $NaBH_4$ in 10 mL deaerated ultra-pure water was added drop wise into the solution under vigorous stirring. After stirring for 2 h a black solid was centrifuged and washed with ultra-pure water several times and dried in oven at 60 °C for 6 h.

2.5 Procedure III: Preparation unmodified of modified carbon paste electrodes

After optimization of the ratio of graphite powder to binder, unmodified carbon paste electrode UCPE was prepared by thoroughly hand mixing the graphite powder and paraffin oil in a ratio 75:25 (w/w) in an agate mortar, using a pestle and then homogenized by dissolving in dichloromethane. The mixture was stirred until all the solvent evaporated. A portion of the resulting homogeneous paste was packed into the cave of the Teflon tube (ca. 2.5 mm i.d.). A copper wire was fixed to a graphite rod and inserted into the Teflon tube served to establish electrical contact with the external circuit.

The multi-walled carbon nanotubes modified carbon paste electrode (MWCPE) was prepared by mixing 75% (w/w) MWCNTs and graphite powder (MWCNT: graphite powder 5:95 %) with 25% (w/w) paraffin oil. The modified composite was then air dried for 24 h and used in the same way as the UCPE.

The modified carbon paste electrode with Pd/MWCNT and Au/MWCNT nanocomposite (Pd/MWCPE and Au/MWCPE) was prepared in the same manner by mixing 75% (w/w) Pd/MWCNT nanocomposite and graphite powder (Pd/MWCNT: graphite powder 5:95 %) with 25% (w/w) paraffin oil. The modified composite was then air dried for 24 h and used in the same way as the UCPE.

The modified carbon paste electrode with Au/Pd/MWCNT nanocomposite (MCPE) was prepared in the same manner by mixing 75% (w/w) Au/Pd/MWCNT nanocomposite and graphite powder (Au/Pd/MWCNT: graphite powder 5:95 %) with 25% (w/w) paraffin oil. The modified composite was then air dried for 24 h and used in the same way as the UCPE. The amount of Au/Pd/MWCNT nanocomposite (in different percentages of 3%, 5%, 10%, and 15%) was optimized.

3. RESULTS AND DISCUSSION

3.1. Characterization of the MCPE

#### 3.1.1 SEM study of Au/Pd/MWCNT nanocomposite

The SEM images of the Au/MWCNT nanocomposite, Pd/MWCNT nanocomposite, Au/Pd/MWCNT nanocomposite are illustrated in Fig. 1. MWCNTs are decorated with Au NPs with an average diameter of 18 nm (Fig 1A) and with Pd NPs with an average diameter of 45 nm (Fig. 1 B). The nanoparticles are well dispersed and embedded throughout the MWCNT matrix. Fig. 1C shows the morphology of Au/Pd/MWCNT nanocomposite. The presence of Au/PdNPs and MWCNT in the nanocomposite has been demonstrated in EDS results in (Fig. 1 D). The interconnected Au/Pd/MWCNT network may establish electrical conduction pathways throughout the whole composite, which is responsible for the electrical conductivity and electrochemical sensing [44].
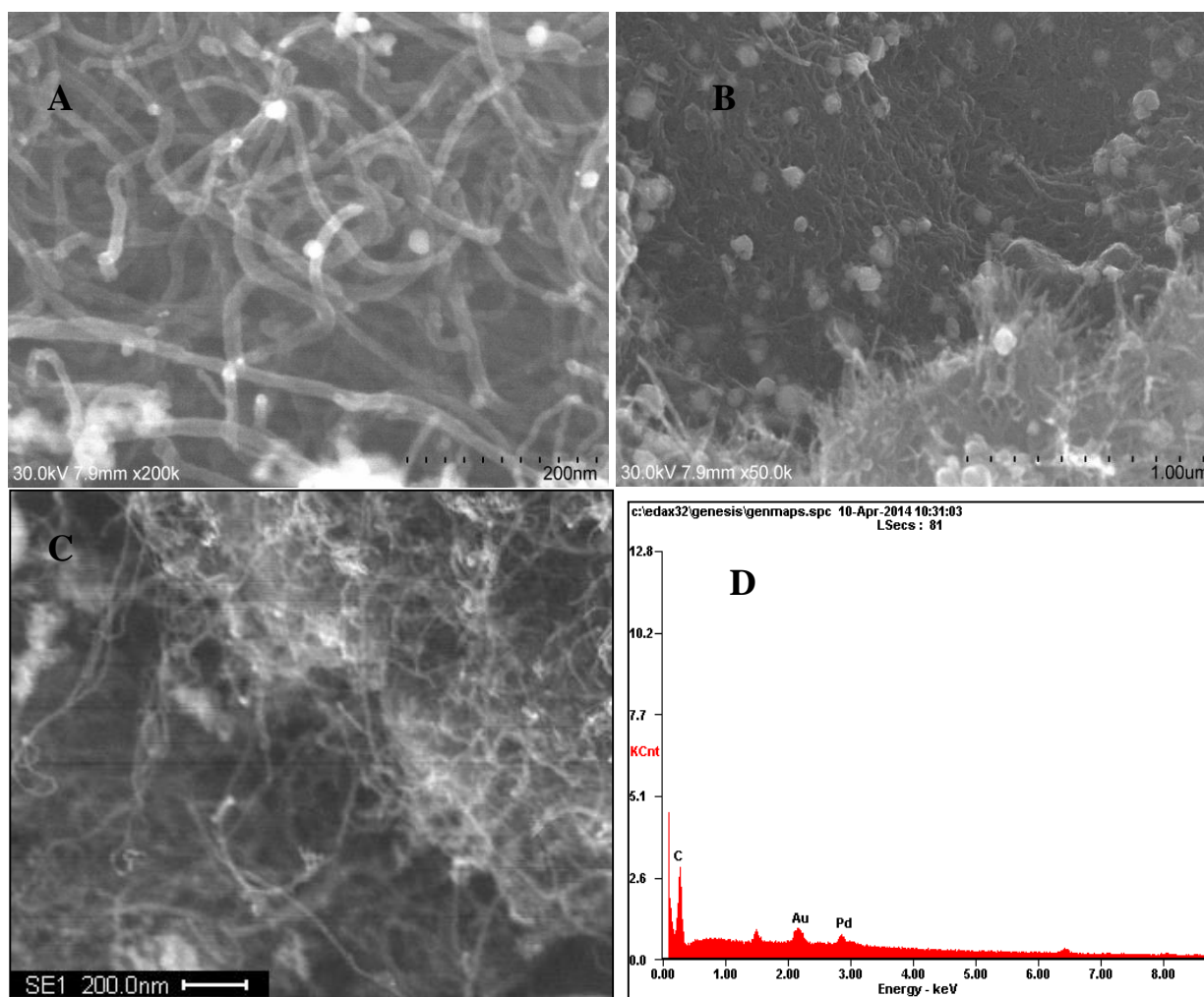
Figure 1. The SEM images of (A) the Au/ MWCNT nanocomposite, (B) Pd/ MWCNT nanocomposite, (C) Au/Pd/MWCNT nanocomposite and (D) corresponding EDS diagram showing peaks for Au/Pd NPs attached to MWCNT.

3.2 Electrocatalytic oxidation study of TM

Fig. 2 shows cyclic voltammograms of UCPE (dashed line) and MCPE (solid line) which were recorded in presence of 1.0×10^{-3} M of TM in B-R buffer solution of pH 2.0 (cyclic voltammograms for MWCPE, Au/MWCPE and Pd/MCPE have not been show to avoid complexity). At the UCPE, the electro-oxidation of TM occurs at approximately 1.038 V with peak current 14.81×10^{-6} A. By modification of CPE with MWCNT, Pd/MWCNT and Au/MWCPE the electro-oxidation of TM occurs at approximately 1.042, 1.040 and 1.040 V with peak current 22.1, 21.7 and 23.5 µA. Electro-oxidation of TM at the surface of MCPE presents an anodic wave with peak current 47.6 µA in a potential near 1.03 V (See Fig. 2) .The obtained results reveals the considerable impact of decoration of MWCNT with Au/PdNPs at promoting of peak current of TM electrooxidation which is due to the effective role of MWCNT as a conductive substrate to present high dispersion of NPs to improve effective surface area. As it can be seen, the peak current increases when PdNPs and Au NPs both exist in MWCNT matrix. It can be concluded, the presence of both NPs with each other shows synergic effect for electro-oxidation of TM.
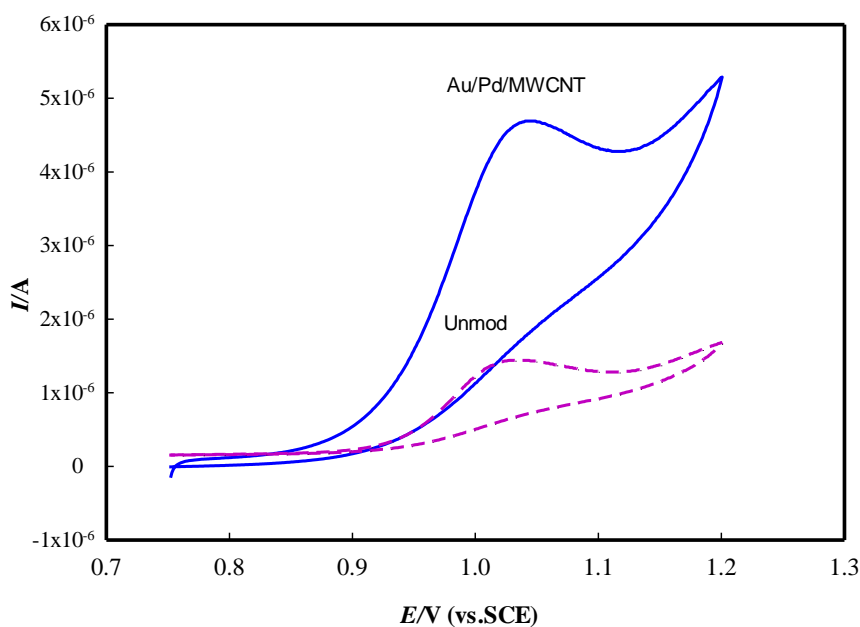

Figure 2. Cyclic voltammograms in the presence of 1.0×10^{-3} M of TM in 0.1 M of B-R buffer solution of pH 2.0 at the surface of UCPE (dashed line), and MCPE (solid line) and scan rate was 0.10 V s^{-1}.

3.2.1. The effect of pH on voltammetric response of TM

The effect of pH on the oxidation of TM was investigated by recording cyclic voltammograms for 1.0×10^{-3} M of TM in the pH range between 2.0 and 8.0at the surface of MCPE (See Fig. 3A). Finding the optimum pH for achieving higher response is important. The peak current decreased with the increasing pH to 3.0 dramatically and then it increased with increasing pH up to 6.0 and finally, the peak current decreased again.The maximum peak current value was observed at pH 2.0 so it was

selected for studying TM in this work (Fig. 3B). As can be seen in Fig. 3C, the anodic peak shifted to less positive values with the increase of pH which shows the pH dependency of oxidation potential of TM. This behavior of TM is in agreement with literature [14].
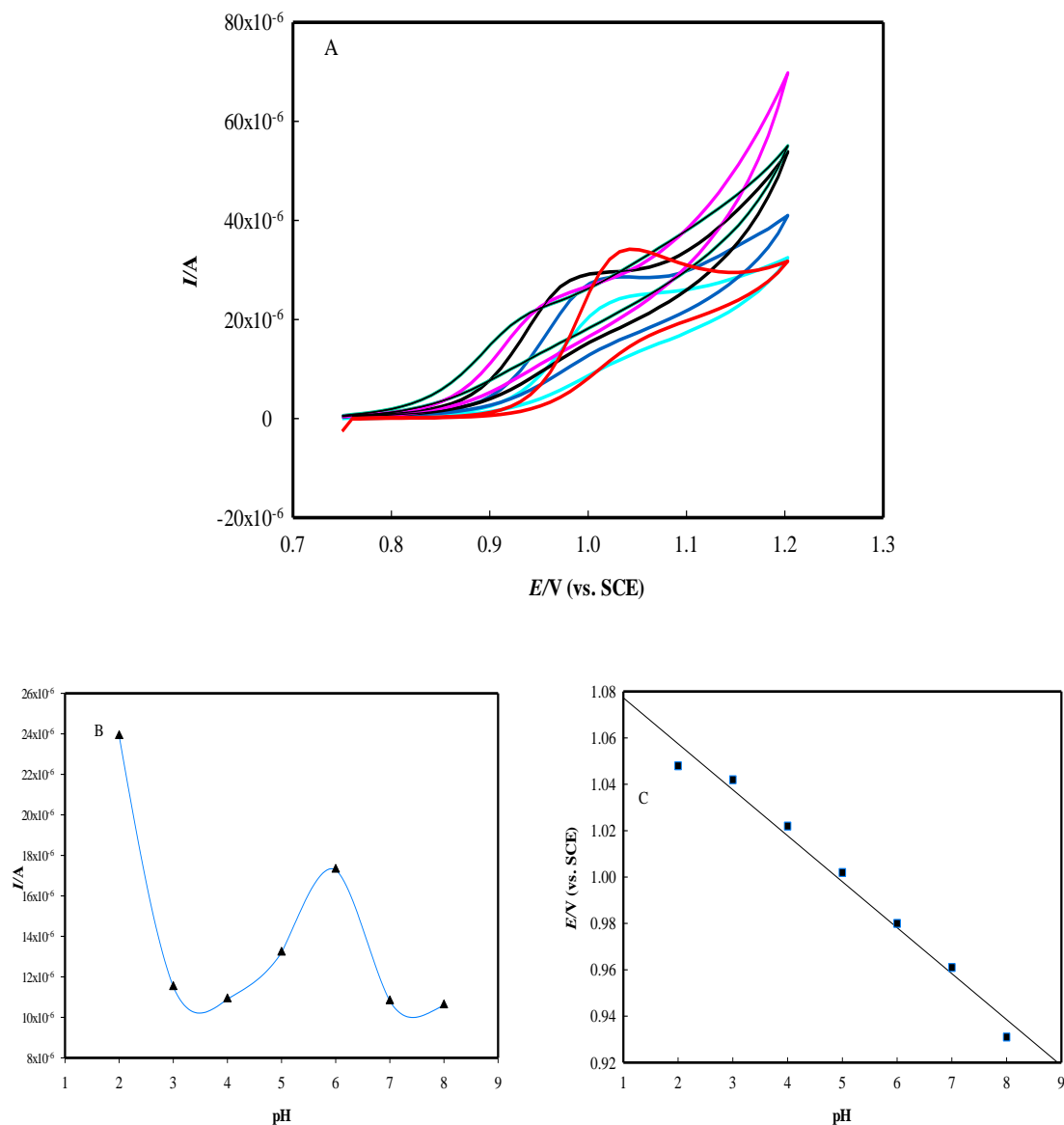
Figure 3. (A) Cyclic voltammograms of TM at the surface of MCPE in B-R buffer solutions pHs 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0. Scan rate was 0.10 V s^{-1}. (B) pH dependency of oxidation peak current of TM (C) pH dependency of oxidation potential of TM.

3.2.2 The effect of scan rate

The effect of scan rate on the peak current of TM was studied. Fig.4A exhibits the cyclic voltammograms of MCPE in 1.0×10^{-3} M of TM (pH 2.0 B-R buffer solution) at various scan rates in

the range of 0.01-0.20 Vs^{-1}. The results showed that the peak current (I_{pa}) varied linearly with the square root of scan rate ($v^{1/2}$) (Fig.4B) which suggesting that the electrooxidation of TM on the surface of MCPE followed a diffusion controlled mechanism in the studied range of potential sweep rates. The linear regression equation was obtained as following equation:

$$I_{pa}/A = 0.0002 \, v^{1/2} / (V \, s^{-1})^{1/2} + 4.0 \times 10^{-5} \qquad (R^2 = 0.991) \qquad (1)$$

In addition, the dependence of $\ln I_p$ on $\ln v$ is linear and obtained as $\ln I_p/A = 0.433 \ln v \, (Vs^{-1}) - 8.27$; $R^2 = 0.993$ (Fig. 4C). Its slope is 0.433, which confirmed the diffusion control of the electron transfer process. A slope close to 0.5 is expected for a diffusion-controlled process [45].
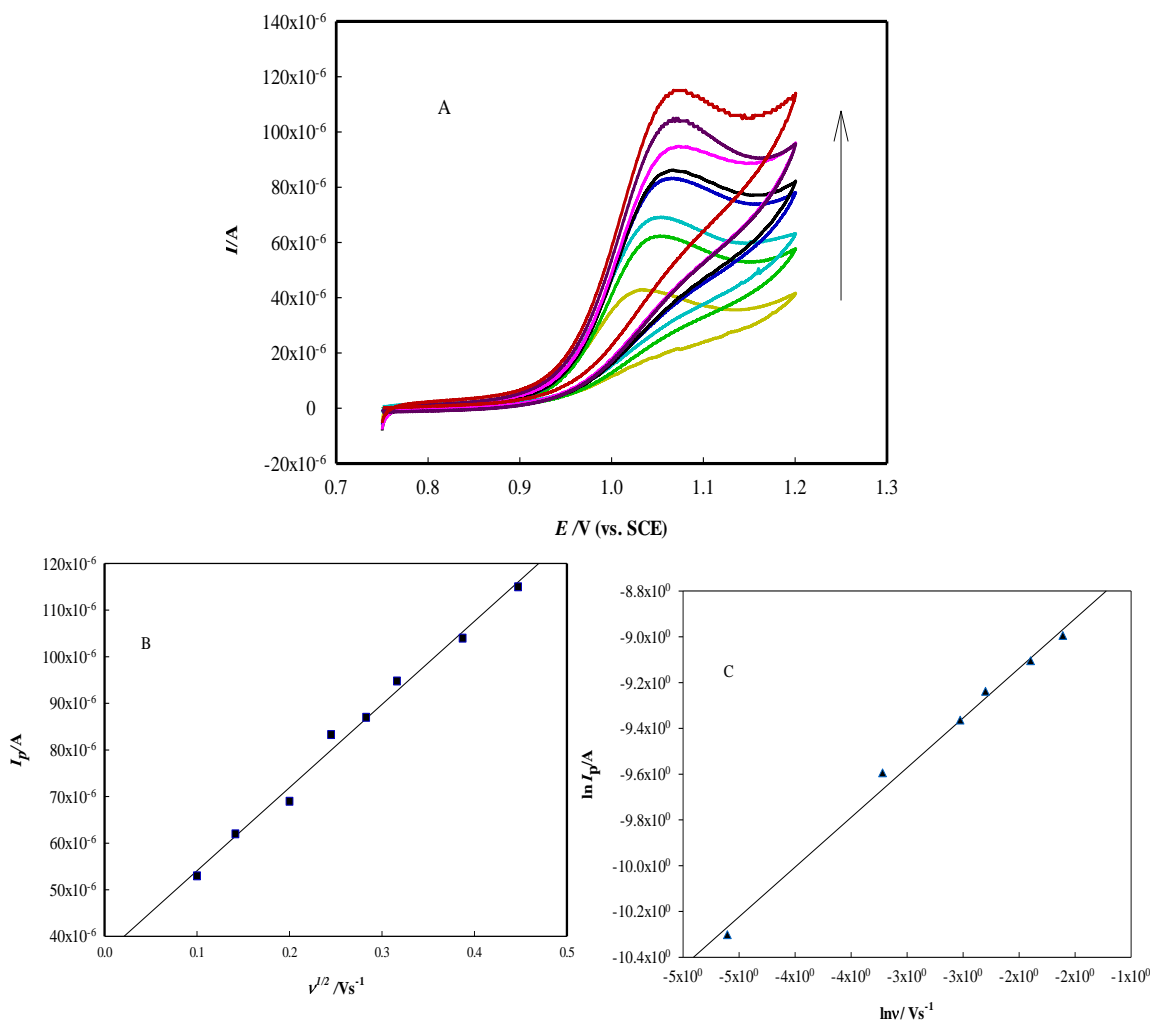

Figure 4. (A) Cyclic voltammograms of 1.0×10^{-3} M of TM at the surface of MCPE at different scan rates (down to top: 0.01, 0.02, 0.04, 0.06, 0.08, 0.10, 0.15 and 0.20 Vs^{-1}) in 0.1 M of B-R buffer solution of pH 2.0. (B) Variation of the electrocatalytic peak current with the square root of scan rate. (C) Variation of the electrocatalytic peak current with the neperian logarithm of scan rate of TM.

The Tafel plot and its corresponding slop were used to obtain the information on the rate determining step. Tafel plot was drawn using the data of rising part of current-voltage curve recorded at a scan rate of 0.2 Vs^{-1} (Fig 5). The slop of Tafel plot is equal to $n (1-\alpha) F/2.3RT$ [45]. In this

condition, the number of electron involved in the rate determining step can be calculated from the slop of Tafel plot which was obtained 9.19 Vdecade-[1] (inset of Fig. 5) .The value of αn_a was obtained 0.54 indicating one electron transfer to be rate limiting (assuming $\alpha=0.5$) in the electrocatalytic oxidation of TM.
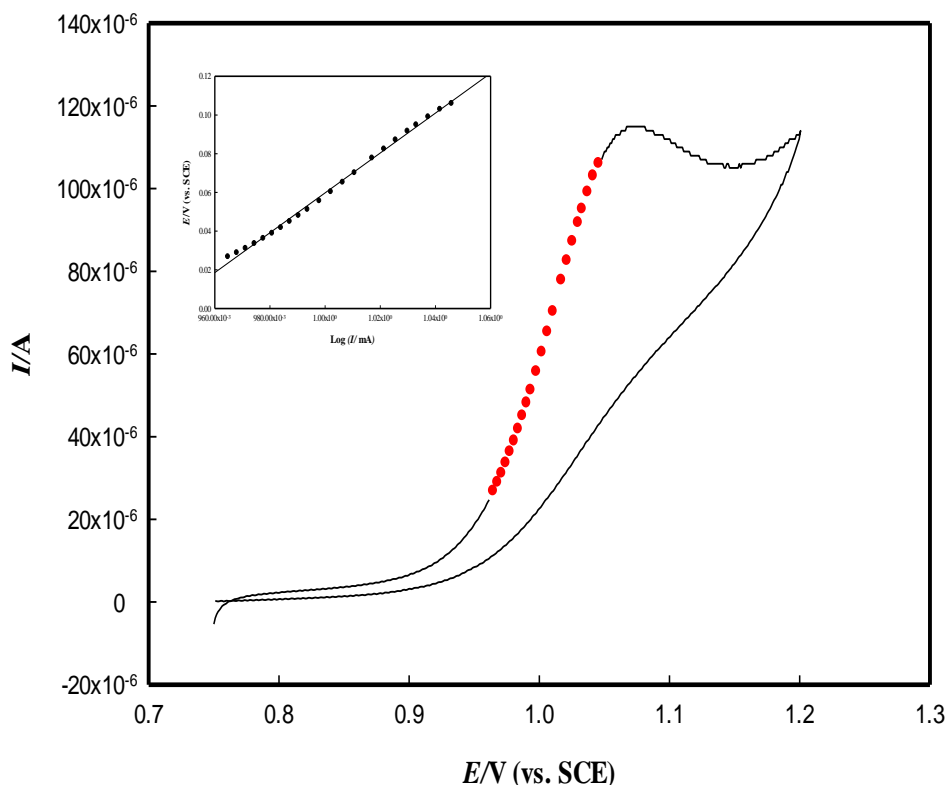

Figure 5. Tafel plot derived from rising part of voltammogram recorded at scan rate 0.20 Vs[-1]in the presence of 1.0×10^{-3} M of TM in 0.1 M of B-R buffer solution of pH 2.0 at the surface of MCPE.

3.2.3 Analytical Results I.: Test Samples

Differential pulse voltammetry (DPV) was applied as a sensitive and reliable method with low limit of detection for measuring trace values of TM in 0.1 M of B-R buffer solution (pH 2.0). Figure 6A shows differential pulse voltammograms of various concentration of TM in the concentration range of 5.0×10^{-9} -1.0×10^{-3} M. The peak current of TM oxidation was increased by increasing the concentration. Two dynamic linear ranges were obtained in concentrations of 1.0×10^{-5} -1.0×10^{-3} M (Eq. 2, Fig 6B) and 5.0×10^{-9}-8.0×10^{-7} M (Eq. 3, Fig. 6C) and the detection limit was calculated to be 5.8×10^{-11} M. The following equations were obtained for the plot of peak current versus the TM concentrations:

$$I_{pa}/A = 11.3 \times10^{-6} + 0.0172\ C_{TM}/M \qquad (R^2=0.994) \qquad (2)$$
$$I_{pa}/A = 2.83 \times10^{-7} + 7.896\ C_{TM}/M \qquad (R^2=0.998) \qquad (3)$$
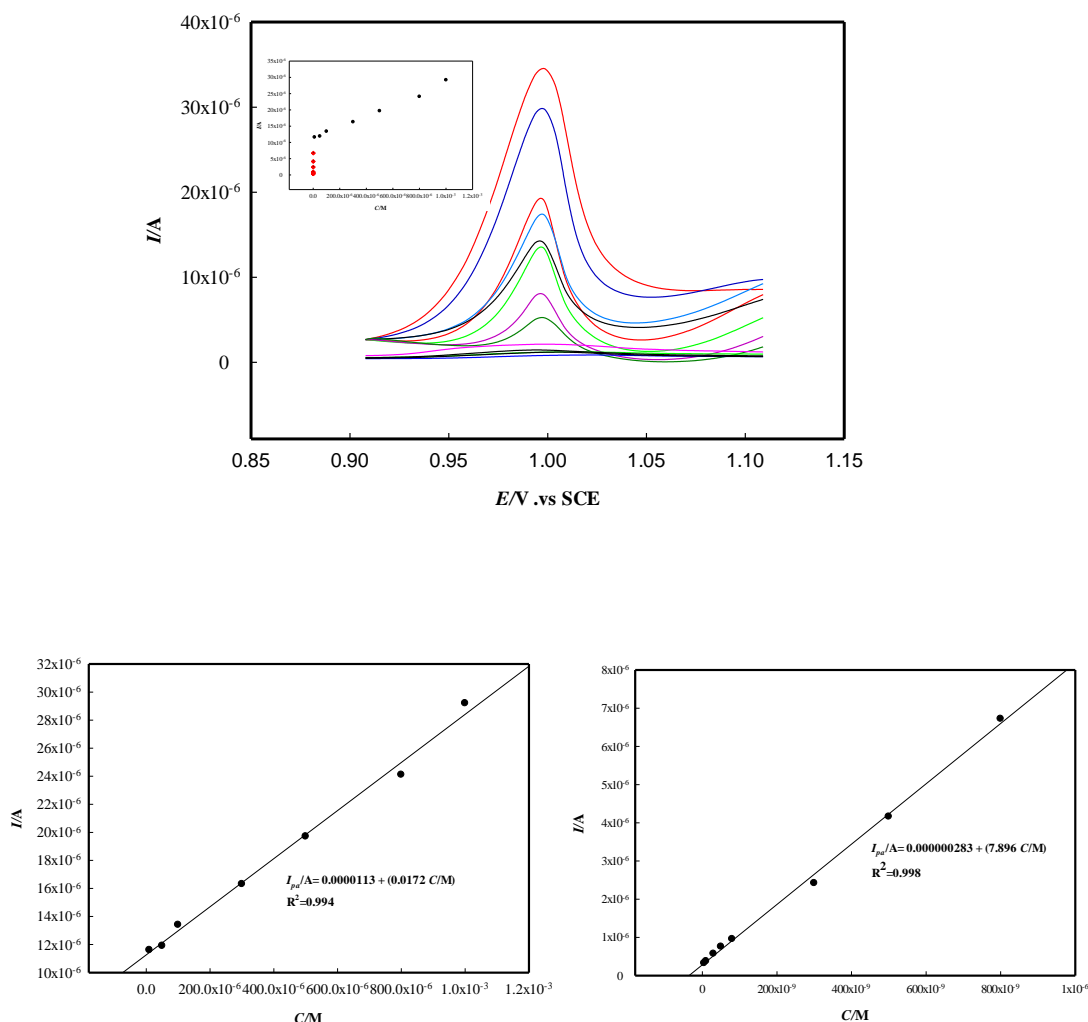
Figure 6. (A) Differential pulse voltammograms of MCPE in B-R buffer solution pH 2.0 containing different concentration of TM, from outer to inner correspond to 1.0×10^{-3}, 8.0×10^{-4}, 5.0×10^{-4}, 3.0×10^{-4}, 1.0×10^{-4}, 5.0×10^{-5}, 1.0×10^{-5}, 8.0×10^{-7}, 5.0×10^{-7}, 3.0×10^{-7}, 8.0×10^{-8}, 5.0×10^{-8}, 3.0×10^{-8}, 1.0×10^{-8}, 5.0×10^{-9} M (B) Variation of the electrocatalytic peak current with the TM concentration in two linear ranges of 1.0×10^{-3} -1.0×10^{-5} M and 8.0×10^{-7} -5.0×10^{-9} M (scan rate 0.10 Vs^{-1}; pulse amplitude 50 mV; step potential 5 mV; Modulation time = 25 mV).

Table 1 compares most electrochemical methods, which were previously used for the determination of TM. In the most of the cases, TM was measured by using adsorptive stripping voltammetry (ACSV) methods. In the presented work, CPE is used instead of mercury electrode which is toxic. In addition, CPE has many advantages compare with mercury electrode such as good reproducibility, stability, easy renewal and good compatibility with different modifiers such as metal NPs with high surface area and electrocatalytic properties have been used to improve the properties of CPE. Compared to other methods, the wider dynamic linear range and noticeable limit of detection were obtained at current work.

Table 1.Comparison of some electrochemical methods that previously used for the determination of TM

Method	Electrode	DLR (M)	LOD (M)	Reference
CCV- FI	Au microelectrode	1.0×10^{-10} -1.0×10^{-8}	1.0×10^{-11}	[2]
AdSV-SWP	HMDE	1.0×10^{-9} -1.2×10^{-8} and 1.2×10^{-8} -1.0×10^{-7}	6.6×10^{-10}	[12]
SWP	HMDE	4.0×10^{-8} -3.0×10^{-6}	2.5×10^{-8}	[12]
AdSV-SWP	HMDE	1.0×10^{-7}-1.5×10^{-6}	1.26×10^{-9}	[13]
DPV	SMDE	1.0×10^{-6}-5.0×10^{-6}	2.5×10^{-6}	[11]
DPV	nanoFe3O4 @GO-GC	2.0×10^{-7}-3.4×10^{-4}	2.0×10^{-8}	[14]
DPV	**Au/Pd/MWNT-CPE**	**1.0×10^{-3} -1.0×10^{-5} and 8.0×10^{-7} - 5.0×10^{-9}**	**5.8×10^{-11}**	**This work**

3.2.4 Analytical Results II: Real Samples

A standard addition method was applied for the determination of TM in the commercially available pharmaceutical sample (eye drop, containing 5.0 mg of TM in 1.0 ml) by using the DPV method. The content of drop samples was diluted with B-R buffer solution of pH 2.0 to prepare an aliquot equal to 1.26×10^{-3} M. The slope of the calibration curve, which is obtained by the spiked standard solutions of TM in the range of 1.0×10^{-3} to 1.0×10^{-5} M, was 0.0175 A/ M with a correlation coefficient of R^2=0.990. According to standard addition plot and comparing two slops of standards and spiked drug samples, a recovery of 98.83% was obtained which indicates the efficiency of the modified electrode for the determination of TM in presence of the matrix of drug sample. Recovery test of TM was carried out by spiking of TM in synthetic serum. The serum sample was spiked with different amount of TM. Recovery has been found to be 104.6 %.

3.3 Reproducibility of sensor preparation

The reproducibility of electrode (by preparing four electrodes with the same method at different days and measuring their peak current) was investigated in the presence of 1.0×10^{-5} M of TM in B-R buffer solution pH 2.0 and potential scan rate 0.01 V s^{-1}. The relative standard deviation based on the average of five measurements per MCPE was 2.95%. The repeatability of the peak current of MCPE

was evaluated with repeating voltammetric measurement ten times with the same MCPE in a 1.0×10^{-5} M of TM solution. The relative standard deviation based on ten measurements was 2.15%.

The electrode response has retained 91.3% of its initial peak current after remaining the MCPE at room conditions for two weeks. These results show good reproducibility and repeatability and long-term stability of the modified electrode in these experiments.

4. CONCLUSION

In this work, the modified CPE with MWCNT which was decorated with Au/Pd NPs applied for preparing a sensitive electrode for detecting submicromolar concentration of TM. The electrooxidation of TM was studied using presented modified electrode for the first time. Satisfactory results of MCPE for determination of TM in pharmaceutical sample, good repeatability and accuracy of results reveal the potential of this presented sensor. In addition, this sensor can be prepared easily and it is stable for a long period.

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