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RESEARCH ARTICLE

Electrochemical sensor based on SmHCF/multiwalled carbon nanotube modified glassy carbon electrode for dopamine

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ABSTRACT

SmHCF/(MWCNT) nano structures modified glassy carbon (GC) electrode was used as electrochemical sensor for the electro oxidation of dopamine. Our strategy was the combination of high electrocatalytic property of SmHCF to electroactive biomolecule and high conductivity, surface area and adhesive properties of carbon nanotubes. The presence of SmHCFnanoparticles and MWCNT were approved by Scanning electron microscopy (SEM) and cyclic voltammetry (CV). The electrocatalytic performance of GC, SmHCF-GC, MWCNT-GC and SmHCF-MWCNT-GC electrodes toward dopamine was compared and the results cleared the enhanced electrocatalytic activity of SmHCF-MWCNT-GC (lowering the potential of the oxidation process and increased oxidation current peak.) relative to others. This unique combination leads to the improvement of the sensitivity of dopamine determination. The differential pulse voltammetry was used for quantitativedetermination of dopamine. The linear dynamic range relationship between oxidation peak currents and dopamine concentration was 2×10^{-7}- 5×10^{-6} (slope = 24.187 µAµM^{-1}) with the detection limit of6×10^{-8} forDA. The sensitivity of the electrode was 24.187 µAµM^{-1} that it is very high relative to reported works. The relative standard deviation (RSD) of the reproducibility (5 modified electrodes), repeatability (successive 10 times), and stability (50 days) of the modified electrode were 3%, 3% and 2.5% respectively. The accuracy and selectivity of the modified electrode were indicated in the real sample as human serum samples and in the presence of possible interfering agents. Good selectivity and recovery were observed for modified electrode.

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INTRODUCTION

One of the important neurotransmitter from catecholamine family in mammalian central nervous is Dopamine (DA), 4-(2-aminoethyl) benzene-1,2-diol. This neurotransmitter has serious function in the control of central nervous, renal, cardiovascular, and hormonal systems. In addition to Parkinson, Alzheimer and Schizophrenia and Schizophrenia disease the dopamine also involved in the drug addiction [1, 2]. DA acts as a local chemical messenger, like a vasodilator, to reduction of insulin production or regulation of lymphocytes activity [3].Hence the exact determination of dopamine concentration in biological fluids is very important. Several techniques such as colorimetry [4], LC–MS/MS [5], HPLC-MASS spectroscopy [6-8], HPLC- fluorescence [9, 10], fluorescence, electrophoresis [11-13] and electrochemical methods [1, 2, 14-16] have been reported for DA determination in various samples.

Among mentioned methods electrochemical techniques have advantages such as, low detection limit, low sample and solvent consumption, low matrix effects upper sensitivity, simplicity, affordability, suitability for real-time detection, reproducibility and high-speed analysis. In electrochemical methods for improvement of

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analytical merits such as sensitivity, selectivity and detection limit the surface of electrodes are physically and chemically modified with suitable modifiers [1, 17, 18].

One of the most favorite modifier groups is metal hexacyanoferrates (MHCFs). These materials as mixed-valence compounds have nice properties and play important role in various areas such as electroanalysisetc [19-25], Electrochromism [26-28], production [29-31], ion exchange [32], ion selectivity [33]. They are also used in biosensors and solid state batteries [34-37].

The low adhesion property of ultrafine nanoparticles limit the using of metal hexacyanoferrates as modifier on the electrode surface, as MHCF particles splash into solution during the analysis process. In sensor using metal hexacyanoferrates materials to prevent the mentioned problem, usually the metal hexacyanoferrates particles are mixed/ or dispersed in suitable wrapper conductive materials. For example composites containing MHCFs such as MHCF-conducting polymers (1) MHCF-graphene oxide/carbon nanotubes (19) MHCF-carbon nanotubes [35],MHCF graphene [23], have been reported for tackle the mentioned problem. Carbon Nanotube (CNT) is one of the important allotrope of carbon (others are the fullerene, diamond and graphene) with a cylindrical structure in nanoscale diameter. The CNTs have attracted much attention since their discovery in 1991 [38]. The high electrical conductivity, high electrocatalytic effect, excellent biocompatibility and strong adsorptive ability are the unique properties of the CNTs [39-42]. Multiwalled Carbon nanotubes (MWCNTs) possess the unique structure and properties including large surface areas, stability and rich surface chemical functionalities[43]. The solar cells, batteries [39], actuators [40, 44-49] and glucose sensing [41] are important industrial applicationsof MWCNTs. Besides the good folder property, of the MWNTs, they act as new electron meditator and promote electron transfer process, especially in the electrochemical reactions [50].

In the current work a simple, facile and rapid route to modification of glassy carbon electrode with MWCNTs and Samarium Hexacyanoferrate (SmHCF) for the determination of DA will be introduced. The good adhesive property of MWCNT (for the improvement of the sensor stability and durability) and good catalytic effect of SmHCF nanoparticles for catalytic oxidation of dopamine were our strategy in this work. The electrode modified in two simple steps process, including the drop casting of MWCNTs on GCE electrode followed by electrodeposition of SmHCF. The prepared electrode was characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectrometry(EDS) and cyclic voltammetry (CV). The MWCNTs/SmHCF modified electrode successfully electrocatalyze the DA and is quantified in the real system serum sample using differential pulse voltammetric (DPV) method. It was found that the modified electrode not only exhibited strong electrocatalytic activity for oxidation of DA but also showed great stability and durability.

EXPERIMENTAL

Chemicals

Dopamine hydrochloride (DA) was purchased from Tehran drug Pharmaceutical Company (Tehran, Iran). All reagents were of analytical grade and were used as received. The DA stock solutions of 1×10^{-2}mol L^{-1} were prepared by dissolving the appropriate amount of this drug in distilledwater in 25 mL volumetric flask. To minimize decomposition, thestock solution was stored in the dark and under refrigeration. Standardsolutions of this drugwith lower concentrationswere prepared daily bydiluting the stock solution with distilled water. All solutions were preparedwithdouble distilledwater. The supporting electrolytewas phosphatebuffer solution (PBS, 0.1 mol L^{-1}, pH 7). Samarium nitrateHexahydrate (99%)was obtained fromAldrich and usedwithout furtherpurification. Sodium chloride (99%) and potassium hexacyanoferatte(99%)were obtained fromMerck. TheMWNTswere bought from Iran'sResearch Institute of Petroleum Industry and synthesized by chemicalvapor deposition (CVD) with a diameter of 8–15 nm, a length of 50 μm and the purity of 95%.

Apparatus

All voltammetric measurements were carried out with a Palm Sens (EmStat instrument 3, The Netherlands) controlled by software PSTrace. A standard three-electrode cell was used for all electrochemical experiments. The bare glassy carbon electrode (GCE) and MWCNTs/SmHCF modified electrode were used as working electrodes. A platinum wire served as a counter electrode and all the potentials were relative to an Ag/AgCl/KCl

(3.5 $molL^{-1}$) reference electrode. The pHs of the solutions were controlled by a Metrohm pH/mV meter M-827 (Switzerland).

Preparation of MWCNTs and electrochemical fabrication of MWCNTs/SmHCF composite modified electrode

The GC electrode was polished carefully with 0.05μm alumina slurry on a polishing cloth, and then washed ultrasonically in ethanol and water, respectively. 0.1mg of the untreated MWNTs was added to 5mL of nitric acid (wt. 65%), the mixture was sonicated for about 3 h to obtain a relatively stable suspension. The cleaned GCE was coated by casting 20μL of the black suspension of MWNTs in nitric acid and dried in an oven at 50 °C to remove the acid. Then the MWNTs modified GCE was washed with water until the remained acid was completely separated(Rezaei et al. 2008). The solution for preparation of the SmHCF, using the electrodeposition method, was a 5 mM$Sm(NO_3)_3$ + 5mM $K_3Fe(CN)_6$ solution containing 0.2 MNaCland freshly prepared each time just before the experiments. The SmHCF was deposited on the surface of the MWNTs /GC electrode by potential cycling from +0.8 to -0.2 V at a sweep rate of 50 mV/s for 20 cycles (about 13 min) in the above solutions. The SmHCF was found to grow on the surface of the MWNTs/GC electrode with each potential cycle, as revealed by the change of peak currents with each cycle. Finally, the electrode was rinsed thoroughly with distilled water [51].

Preparation of Human Serum Sample

Determination of DA was carried out on human serum sample. The prepared modified electrode was applied to the analysis of the human serum samples using the standard addition method. The serum sample was initially centrifuged. After filtering, the sample was diluted 10 times with 0.1 M phosphate buffer of pH 7.0 [52]. The diluted serum sample was spiked with different amounts of standard DA. Finally, after 30 min its DPV was recorded using the modified electrode.

RESULTS AND DISCUSSION

Electrodeposition of SmHCF on the surface of the MWCNTs/GC electrode

A solution of 5 mM$Sm(NO_3)_3$, 5 mM $K_3Fe(CN)_6$ and 0.2 M NaCl (as supporting electrolyte) was used for synthesis of SmHCF nanoparticles. The SmHCF nanoparticles were deposited on MWCNTs/GC electrode surface by cyclic voltammetry technique (Fig. 1). It is clear that the redox peak currents of the $Fe(CN)_6^{3-/4-}$ couple is decreased gradually with the increase of the scan cycles, which confirms the formation of SmHCF on the electrode. In other word the potential of SmHCF formation overlapped with the potential of $Fe(CN)_6^{3-}$/ $Fe(CN)_6^{4}$ reaction. The Sm^{3+} ion reacted instantaneously with $Fe(CN)_6^{4-}$ to form and deposit of SmHCF on the electrode surface. The mechanism of SmHCF formation on electrode surface is as the following EC reaction mechanism.

$Fe(CN)_6^{3-} + e^- \longrightarrow Fe(CN)_6^{4-}$(electrochemical reaction) (1)

$Fe(CN)_6^{4-} + Sm^{3+} + Na^+ \longrightarrow NaSmFe(CN)_6$ (chemical reaction) (2)

SEM

Fig. 2 (a,b) shows SEM images of the MWCNTs/GC and SmHCF/MWCNTs/GC modified

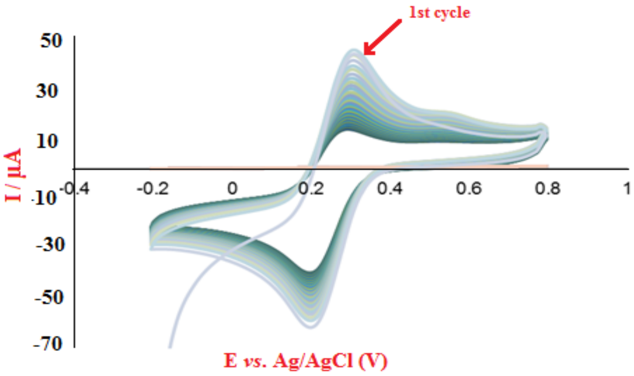


Fig 1. Voltammograms of the SmHCFelectrodeposition on the surface of the MWCNTs/GC electrode in a solution of 5 mM$Sm(NO_3)_3$, 5 mM $K_3Fe(CN)_6$, and 0.2 M NaCl.

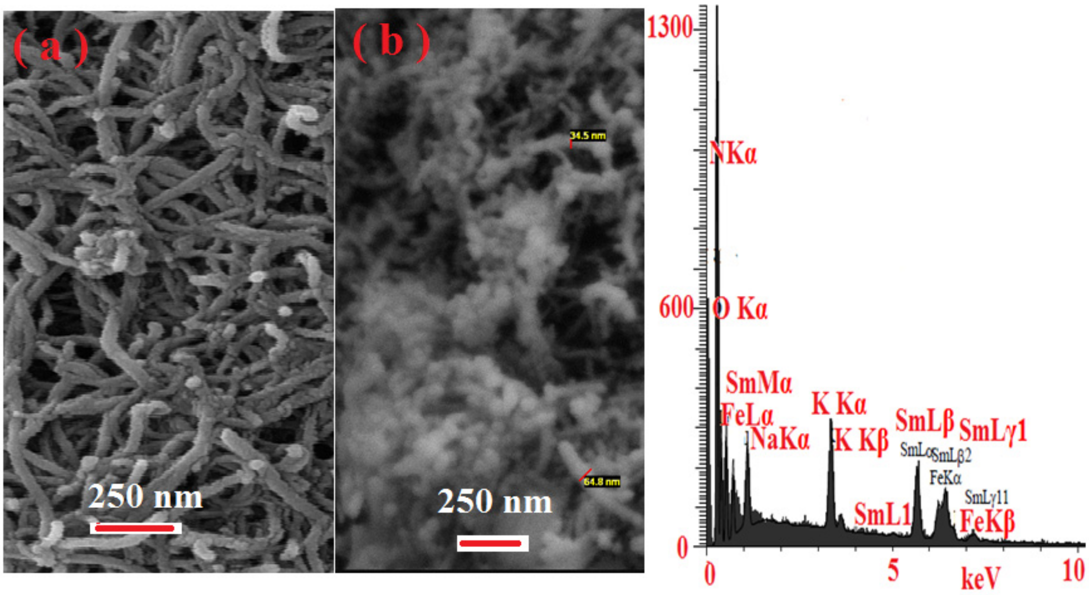


Fig. 2 SEM images of GC electrode modified with (a) MWCNTs and (b) SmHCF/MWCNTs; EDS spectra (inset)

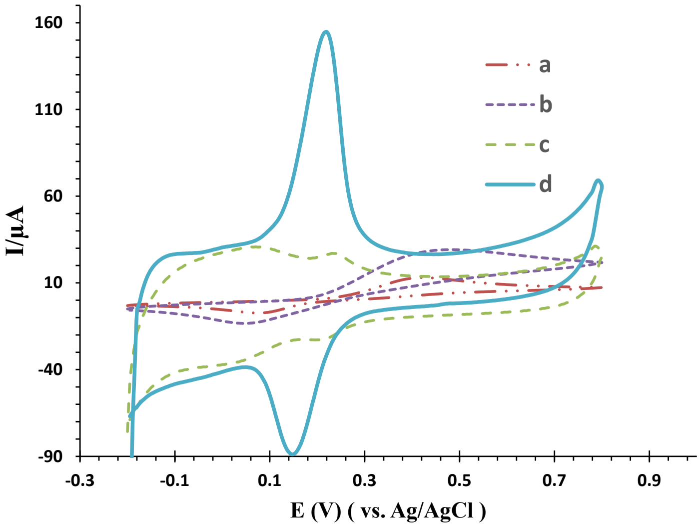


Fig. 3 Cyclic voltammograms of (a) bare, (b) SmHCF modified, (c) MWCNTs modified, and (d) SmHCF- MWCNTs modified GC electrode sin 0.1 M phosphate buffer solution (pH 7.0) in the presence of 1× 10 $^{-5}$ M of DA

electrode. Fig. 2a shows image of MWCNT modified electrode, as can be seen the surface of glassy carbon electrode has been uniformly covered by nanotubes uniformly (by well dispersed in nitric acid no entwined of nanotubes was taking place).Fig. 2b shows the surface morphology of the SmHCF-MWCNTs modified electrode. To approve the presence of SmHCF nanoparticles on the electrode surface, the EDS was performed on electrode surface. Fig. 2 (inset) shows the EDS spectra of modified electrode, in the spectrum the peaks of Sm, Fe elements are shown clearly.

Catalytic oxidation of Dopamine at the SmHCF/MWCNTs/GC modified electrode

A bare GC, SmHCF-GC, MWCNTs -GC and SmHCF-MWCNTs-GC electrodes were used for the study of the electrochemical behavior of DA in 0.1 M phosphate buffer solution (pH 7.0) contain of 1× 10 $^{-5}$ M of DA (Fig. 3). as can be seen, it is clear that the bare GC, MWCNTs -GC and SmHCF-GC electrodes do not show an indicated redox peaks for

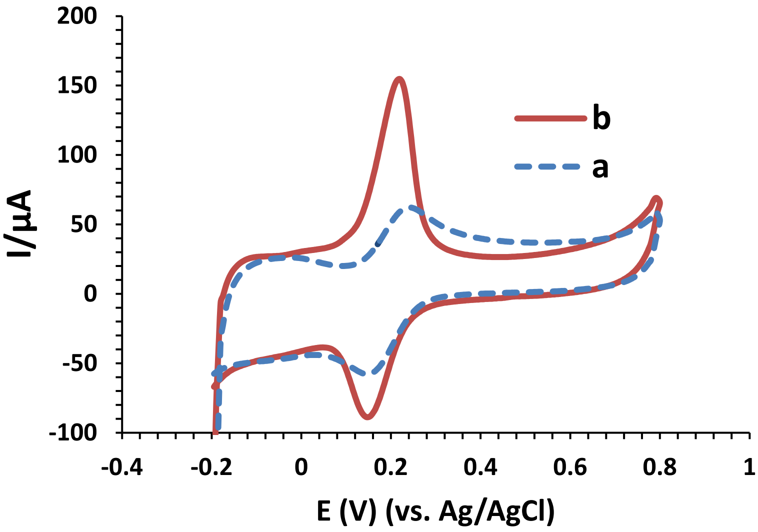


Fig. 4 Cyclic voltammograms of SmHCF- MWCNTs modified GC electrode sin 0.1 M phosphate buffer solution (pH 7.0) in (a) absence and (b) presence of DA (1×10^{-5} M).

DA. While a sharp redox peak of DA at +0.22 V on SmHCF/ MWCNTs electrode, can be seen clearly which confirm the electrocatalytic property of SmHCF/ MWCNTs electrode toward DA species. The instability of SmHCF modified electrode and splashing of SmHCF particles into solution during work is the absolute reasonbehind of absence of redox peaks of DA on SmHCF- electrode. The improved and boosted redox peaks of DA at +0.22 V on SmHCF/ MWCNTs modified electrode are due to the synergistic effect of SmHCF and MWCNTs. The voltammograms of SmHCF/ MWCNTs electrode in the absence and presence of DA (1×10^{-5} M) are recorded in 0.1 M phosphate buffer solution with pH 7.0 as supporting electrolyte (Fig. 4). In the absence of DA or a blank solution (curve a), the redox peak was not observed in the potential range of -0.3 to 1.0 V which clarified that the SmHCF and MWCNTs were non-electroactive in this potential window. When 1×10^{-5} M of DA was dropped to blank solution (curve b) a sensitive and an apparentanodic peak in 0.22 V was observed, which confirms theelectrocatalitic oxidation of DA by SmHCF- MWCNTs-GC electrode.

Scan Rate

For a study of the reaction kinetics, the DA redox peak on the SmHCF-MWCNTs–GC at the different scan rates (**ʋ:** 20-500 mV/s) were recorded (Fig. 5a).

The results indicated that an oxidation and a reduction peaks are present in all scan rates, confirming irreversibility of DA behavior on SmHCF-MWCNTs–GC electrode. Also the results show that anodic current increased linearly by increasing the scan rate and potential positively shifted gradually). The relationship between peak current and log **ʋ** was linear, indicating the DA reaction on electrode is an adsorb-controlled irreversible process. The relationship (linear) between peak currents and scan rates is as following equation:

$$\mathbf{I_{pa} = 0.982\ log\upsilon + 0.1579\ (I_{pa}\ in\ \mu A,\ \upsilon in\ mV\ s^{-1},\ R^2 = 0.991)}$$

pH Effect on Voltammetric Responses

It is well known that the pH of the supporting electrolyte has an important effect on the electrooxidation of DA at the electrode surface. Different pH values ranging from 5.8–8.5 in a 1 $\times 10^{-5}$ M solution of DA were selected for study of pH influence on voltammograms the potentialscan rate was 100 mV s^{-1} (Fig.6). The results show that the peak potential has negative shift with increasing pH, which suggests that H^+ participates in the oxidation process. The maximum anodic peak current was observed at pH 7.0 (Fig.6a). Therefore, pH 7.0 was chosen for further studies of DA. At the 5.8 - 8.5pH range a good linearrelationship was observed between the E_{pa} and the pH values (Fig 6b), the relationship can be expressed as following:

$$\mathbf{E_{pa}\ (mV) = 0.6794 - 0.0628\ pH \qquad R^2 = 0.9930}$$

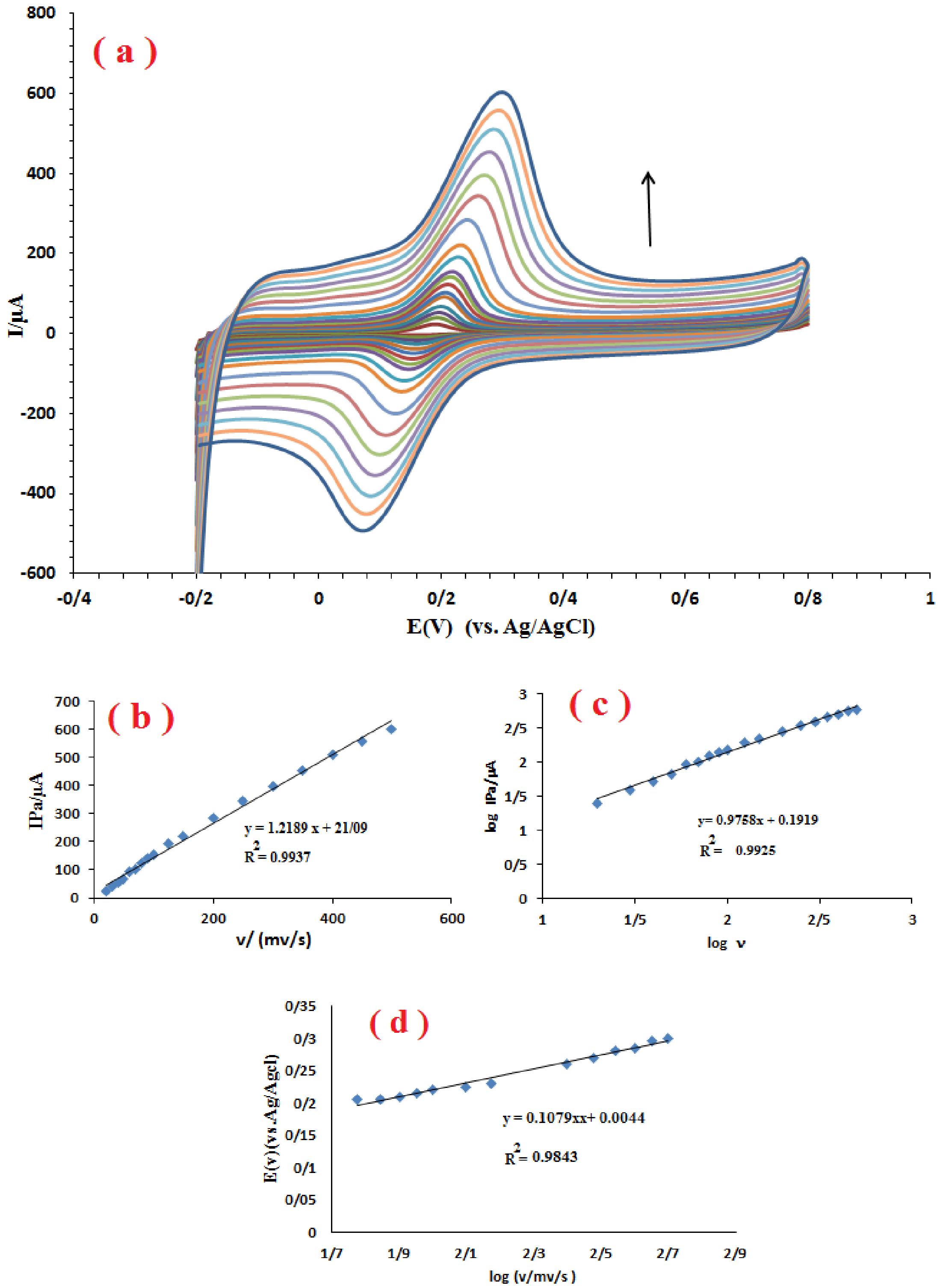
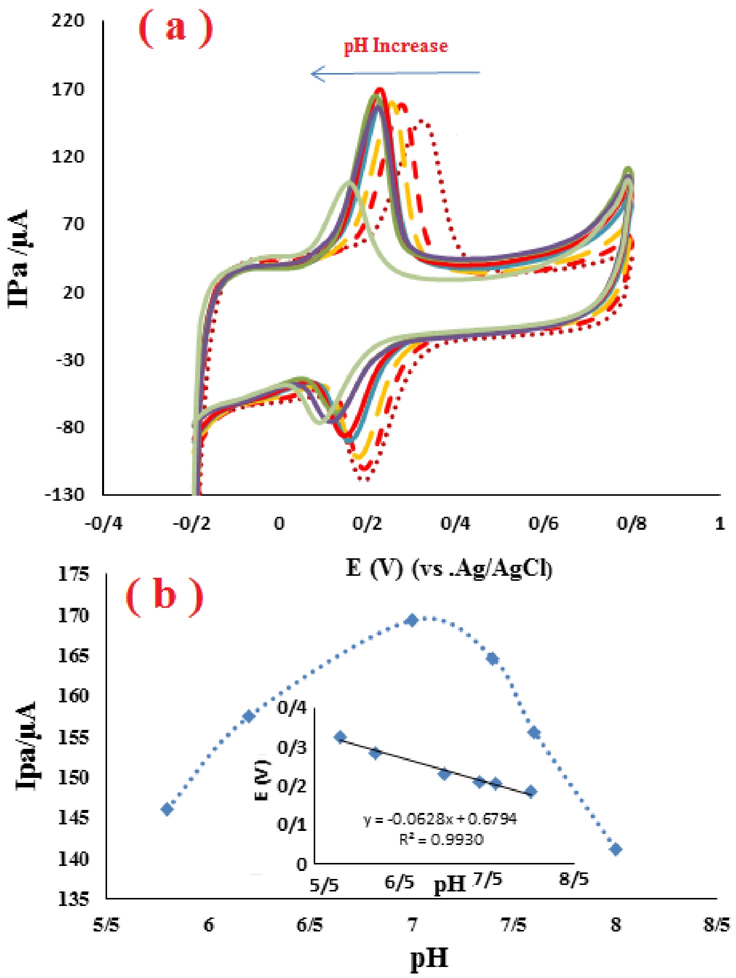


Fig. 5(a) CVs at different scan rates for the SmHCF- MWCNTs modified GC electrode in 0.1 M PBS (pH 7.0). (b) Peak current vs. scan rate plot; (c) plot of log (peak current) vs. log (scan rate); plot of E(v) vs. log(v/mv/s).



(Fig.6). CVs of 1×10^{-5} M DA recorded at 5.8–8.5 range and a scan rate of 100 mV s^{-1}. (a) Plot of the anodic peak current versus the pH value, (b) plot of the anodic peak potential versus pH

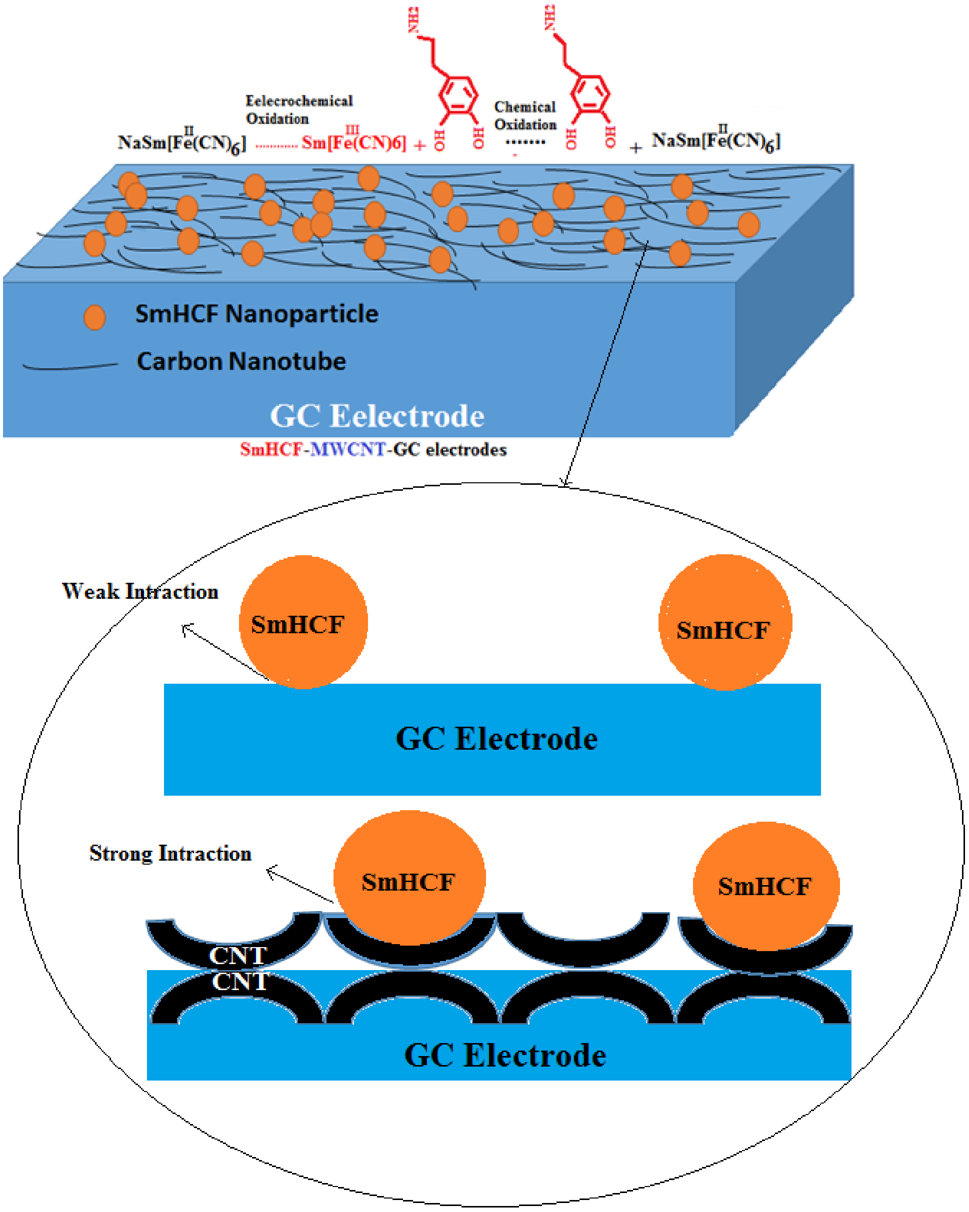
The slope of the linear curve of E_{pa} vs. pH was approximately equal to - 0.0628mV *vs.* pH unit which is close to the expected value of 0.059 mV *vs.*pH. This shift indicates that equal numbers of electrons and protons are involved in the oxidation of DA on the SmHCF-MWCNTs–GC surface. According to the results, and reports the following mechanism was suggested for oxidation of DA. (Scheme 1) (1).

Influence of Accumulation Time

The cyclic voltammetry was used for studying the influence of accumulation time on intensity of oxidation current peak. As can be seen from Fig. 7, the anodic current is increased with accumulation time up to 210 s and then is decreased. The decrease of the oxidation peak after 210 s indicates completely saturation of electrode surface at 210 s and DA desorption after then. So, the accumulated time of 210 s was considered as an optimum time for subsequent experiments.

Differential pulse voltammetric determinations

The DPV technique by modified electrode was used to determination of DA in 0.1 M phosphate buffer solution (pH 7.0). The influence of electrochemical parameters such as, pulse amplitude, pulse width, and scan rate were studied. The best result (high sensitivity) was obtained under condition of: 50 mV, 50 ms, and 30 mVs^{-1} for pulse amplitude, pulse width, and scan rate, respectively. The DPVs at various concentrations of DA are shown in Fig. 8a. The linear relationships between oxidation peak currents (I_{pa}) and DA



Scheme 1. Electrooxidation mechanism of DA

concentration was: 2× 10^{-7} - 5× 10^{-6} (slope = 24.187 $\mu A \mu M^{-1}$), with a detection limit of6× 10^{-8} forDA. The linear regression equation was:

$$I_{pa}\ (\mu A) = 24.187\ C_{DA} (\mu M) + 11.581 \qquad R^2 = 0.9907$$

The sensitivity, linear concentration ranges anddetection limits of modified electrode for the determination of DA were compared with reported sensors (Table 1). As can be seen the sensitivity of our modified electrode is very higher than other biosensors, the sensitivity was 24.187 $\mu A \mu M^{-1}$. Sensitivity is a very important sensor factor. The linear concentration rang and detection limits are acceptable.

Reproducibility, Repeatability, and Stability of the SmHCF/MWCNTs/GC electrode

The stability, repeatability and reproducibility of the modified electrode were determined as

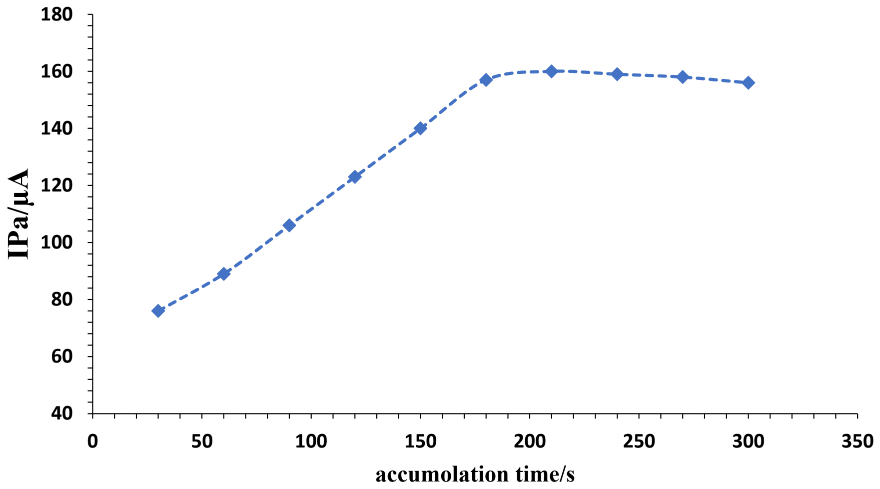


Fig.7 Influence of accumulation time of the oxidation peak currents for DA at modified electrode

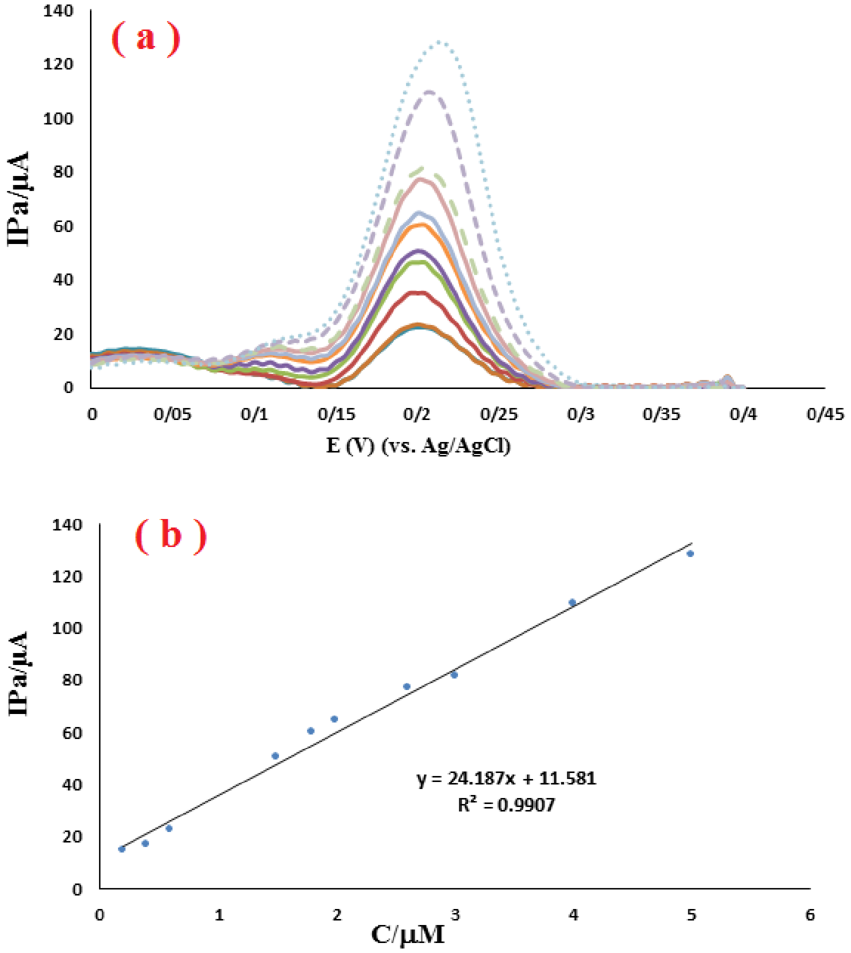


Fig.8 (a) Ads- Differential pulse voltammograms of SmHCF/MWCNTs/GC electrode in PBS (pH 7.0) for the successive additions of DA, (b) plot of peak current as a function of the concentration of DA. [Scan rate 30 mV s^{-1}; pulse amplitude 50 mV; pulse width 50 ms].

Table 1. Comparison of the efficiencies of various electrodes in the determination of DA.

Working Electrode	Technique	Linear Range	Detection Limit	senstivity	Reference
NG/NiTsPc/GCE	DPV	0.1-200	0.1	0.926	[53]
RGO-Pd-NPs/GCE	LSV	1-150	0.233	0.00262	[54]
GNS/PEI/AuNP/GCE	DPV	1-83	0.2	0.2	[55]
MWCNT-nanoFeTSPc/GCE	SWV	0-60	0.098	0.314	[56]
SDS micelles/CPE	DPV	8–134	3.70	0.106	[57]
PG/GCE	CV	5-710	2.0	0.1125	[58]
SGN/NiPc	DPV	40-1080	0.26	0.104	[59]
NiHCF–PNH/Au	DPV	0.01-10	0.021	3.27	[1]
SmHCF/MWCNTs/GCE	DPV	0.2-5	0.06	24.187	This work

Table 2. Effect of interferences on the determination of DA (50 μM) on modified electrode..

Interfering agent	Concentration (mM)	Signal change (%)
Zn^{2+}, Mg^{2+}, K^{+}, Na^{+},	5	<0.3
Cl^{-}, NO_3^{-}, PO_4^{3-}	5	<1.0
Glucose	3	+4.5
Urea, uric acid	10	+3.0
Ascorbic acid	5	+2.0

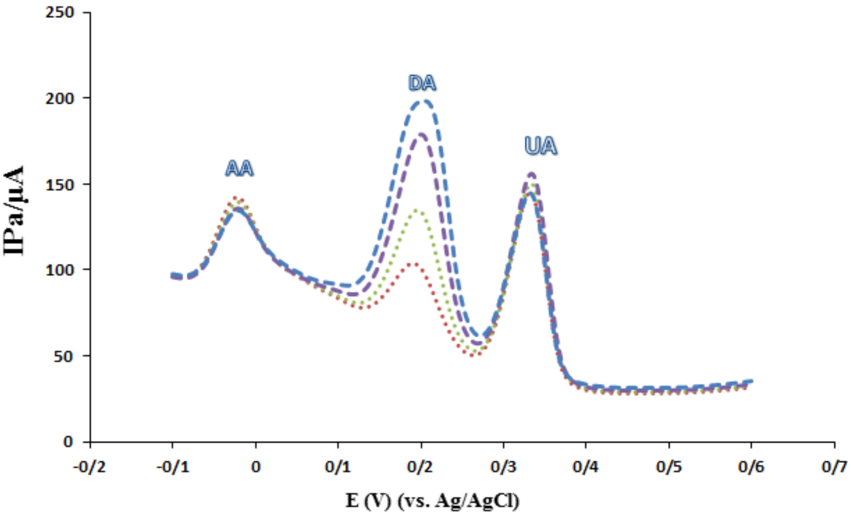


Fig.9 Differential pulse voltammograms of SmHCF/MWCNTs/GC electrode in PBS (pH 7.0) for the DA, in presence of AA and UA

following. For study of electrode stability the DPVs of 50 μM DA solution were recorded over 50 days (every 10 days). The relative standard deviation (RSD) of DA oxidation peak after 50 days was 2.5%, which suggested satisfactory long time stability of the electrode. The repeatability of the response of the modified electrode, was determined in a solution of 50 μM DA repeatedly for successive 10 times and the calculated RSD was 3%, which showed logical repeatability of modified electrode. For study of inter-day reproducibility of the modified electrode 5 modified electrodes were prepared at different days with a same preparation methods. The RSD value for the peak current of 50 μM DA with these electrodes was obtained as 3%, which showed satisfactory reproducibility of modified electrode.

Interference studies

The selectivity of modified electrode was studied in the presence of the possible interfering agents influencing the determination of DA in

Table 3 Determination of DA in the serum samples used the modified electrode.

serum	Added (µM)	Found (µM)	Recovery (%)
1	0.50	0.47 (±0.02)	94.00
2	1.00	0.97 (±0.03)	97.00
3	20.00	20.20 (±0.05)	101.00
4	50.00	52.00 (±0.04)	104.00
5	100.00	103.00 (±0.03)	103.00

solution 50 µM DA. Usually the interfering is serious when it changes the target signal more than 5%. Table 2 shows the results of typically ions and biomolecules which present beside of DA in the real samples and have interference potential in DA determination. It is clear that the oxidation peak current of DA was not affected seriously by substantial addition of cations, anions and organic molecules. Two compounds that commonly found with DA and could more potentially interfere with the determination of DA are UA and AA. The influence of UA and AA were studied under the optimum conditions (Fig. 9). Thus the results demonstrated the sufficient selectivity of modified electrode in the voltammetric determination of DA.

Real sample analysis

For determining the sensor's ability of modified electrode in the real samples, the determination of DA in human serum was studied. The content of DA in the sample was estimated by applying

DPV method. The results are summarized in Table 3. As can see the electrode shows satisfactory ability in real samples.

CONCLUSION

The highest synergistic activity for dopamine oxidation was observed with modification of glassy carbon (GC) using of $Sm[Fe(CN)_6]$ nanoparticles and multi wall carbon nanotube. The roles of $Sm[Fe(CN)_6]$ nanoparticles and MWCNT were considered as electrocatalyst and binder respectively. In the absence of SmHCF nanoparticles the electrocatayist property was not observed. Also the absence of MWCNT the stability of electrode was low and $Sm[Fe(CN)_6]$ splashed to solution. The modified electrode was characterized with Scanning electron microscopy (SEM) and cyclic voltammetry (CV). The modified electrode shows improved electrocatalytic activity for electrochemical oxidation of dopamine. The dopamine concentration was determined by differential pulse voltammetry. The linear dynamic range relationship between oxidation peak currents and dopamine concentration was 2×10^{-7} - 5×10^{-6} (slope = 24.187 $\mu A \mu M^{-1}$) with the detection limit of 6×10^{-8} forDA. The outstanding analytical merits of current work was sensitivity of the modified electrode: 24.187 µAµM-1 that it is very high relative to reported works. The accuracy of the modified electrode was investigated in human serum as the real sample and the selectivity of modified electrode was studied in the presence of possible interfering agents and satisfactory results were observed.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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