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Polyaniline–multi-wall-carbon nanotube nanocomposites as a dopamine sensor

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Abstract: A composite of polyaniline with multi-wall-carbon nanotubes (PANi/MWCNTs) was synthesized by an *in situ* chemical oxidative polymerization method. The PANi nanoparticles were synthesized chemically using aniline as the monomer and ammonium peroxydisulfate as the oxidant. The nanocomposites were prepared as a carbon paste using functionalized MWCNTs and PANi nanoparticles. The PANi–MWCNTs were characterized physically using scanning electron microscopy (SEM) and the electrochemical behavior of the composites in acidic solution (HCl) was investigated using cyclic voltammetry. The PANi/MWCNT composite electrode was used for studying dopamine (DA) as an electroactive material. The cyclic voltammetric results indicated that multi-wall carbon nanotubes (MWCNTs) significantly enhanced the electrocatalytic activity in favor of the oxidation of DA. The kinetics of the catalytic reaction was investigated using the chronoamperometry technique where by the average value of the diffusion coefficient (D) and the catalytic rate constant (k) for DA were determined to be $(7.98 \pm 0.8) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and $(8.33 \pm 0.072) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively.

Keywords: multi-wall-carbon nanotubes; dopamine; nanocomposite; polyaniline; sensor.

INTRODUCTION

Carbon nanotubes (CNTs) are an important group of nanomaterials with unique electronic and chemical properties. Since CNTs were discovered in 1991 by Iijima *et al.*,¹ there has been a growing interest in nanotubes for several applications.^{2–6} CNT-modified electrodes promote electron transfer due to their conductivity and mechanical properties. Composites of a conducting polymer and CNTs show synergistic effects and have been made for different applications. The two types of CNTs, single-wall carbon nanotubes (SWNT) and multi-wall

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carbon nanotubes (MWCNTs), have considerable potential in the field of polymer composites.^{7,8} Functionalized nanotubes are also more easily dispersed in organic solvents, leading to an improved dispersion and homogeneity of the MWCNT within the polymer composite. For this reason, the MWCNTs prepared in these studies were treated with a mixture of concentrated H₂SO₄:HNO₃.⁹

Dopamine (DA) is an important neurotransmitter of the central nervous system. Variations in DA levels may result in brain disorders, such as Parkinson's disease, and also have impacts on learning and memory.¹⁰ Hence, there is considerable interest in developing simple and accurate electrochemical techniques for measuring the chemical behaviors of DA.^{11–14}

The advantages of using conducting polymers as opposed to the historically used inorganic materials are their diversity and ease of synthesis. Conducting polymers have also been studied intensively for their transducing properties.^{15–18} Among those studied, PANi is one of the more important polymers due to its electrical conductivity and stability. Furthermore, it exhibits significant redox behavior. The conducting form of polyaniline is the protonated polyemeraldine or the green-colored polyemeraldine salt with a conductivity of approximately 15 S cm⁻¹.

PANi may be synthesized either chemically or electrochemically. The chemical synthesis involves mixing aniline with an acidic medium, such as HCl or H₂SO₄, and an oxidant, such as ammonium peroxydisulfate, whereas the electrochemical synthesis of PANi may be performed using galvanostatic, potentiostatic or potentiodynamic methods. Recently, the manufacture of CNTs in polymer materials, particularly composites based on polymers and nanotubes, have attracted much attention due their superior properties.^{19–21}

Chemical polymerization is a simple and robust strategy for the large scale production of PAN. When performing chemical polymerization, oxidizing agents, such as ammonium peroxydisulfate, ammonium vanadate, potassium iodate and potassium dichromate, are employed.

There are many articles reporting experimentation concerning the determination of the concentration of DA. Compared with other electrodes^{22,23} used for detection of DA, the proposed sensor shows a long lifetime, a linear dynamic range and good performance. In addition this sensor shows good stability and involves a simple construction. In this study, the electrochemical behavior of a PANi–MWCNTs composite prepared by chemical polymerization was assessed for the measurement of DA.

EXPERIMENTAL

Chemicals and reagents

Multi-wall carbon nanotubes (specific surface area, 250 m² g⁻¹, diameter, 10 nm, length, 10–20 μm) made by chemical vapor deposition (CVD) were provided by the Petroleum Research Institute of Iran. The purity of the pristine MWCNT was 97%. Dopamine, aniline mo-

monomer and ammonium peroxydisulfate were purchased from Merck and used for PANi preparation. All other chemicals and solvents were of analytical grade and were used without any further purification.

Apparatus

All electrochemical experiments were performed at 25 ± 1 °C using a potentiostat/galvanostat Autolab, system type III. A conventional three-electrode cell was used for the electrochemical experiments. Ag/AgCl, platinum wire and PANi–MWCNT composite electrodes were used as the reference, auxiliary and working electrode, respectively. A centrifuge system (Eppendorf, Germany) was used for the physical separation of the MWCNTs.

Microstructure characterization of the PANi–MWCNT composites was performed using a Philips–XL30 low vacuum scanning electron microscope located in Tarbiat Modarres University, Tehran, Iran.

Carboxyl group functionalized MWCNTs

Formation of carboxylic acid groups at the defective sites of the MWCNTs improved their solubility in HCl solution. The prepared MWCNTs were treated ultrasonically using a 3:1 mixture of 6 M H_2SO_4 and HNO_3 at 50 °C for 4 h. The dark suspension was then centrifuged for 30 min at 4000 rpm, washed with distilled water and dried at 50 °C.

Synthesis of the PANi–MWCNTs nanocomposite

The nanocomposite of protonic acid doped polyaniline with functionalized NTs (c-MWCNT) was synthesized using *in situ* chemical oxidation polymerization. This procedure entailed dissolving 0.10 g of c-MWCNT in 50 mL of 0.50 M HCl solution under stirring. The dark c-MWCNT suspension was then added to a solution composed of 0.70 g aniline monomer dissolved in 50 mL of 0.50 M HCl in an ice bath at 0–4 °C and stirred. Ammonium peroxydisulfate (APS) was added drop-wise into the c-MWCNT/aniline solution, and the resulting green suspension was then filtered and dried at 50 °C for 2 h.

For optimization of the modifier, different quantities of MWCNT (0.040, 0.080, 1.0 and 1.4 g) were used while keeping the weight of aniline monomer constant at 0.70 g. Optimization was also attempted using different amounts of aniline monomer (0.30, 0.50, 0.70 and 0.90 g) with a constant amount of CNT (0.10 g). Experimental results showed that a steep rise in peak current occurred when the amount of CNT incorporated into the mixture was increased up to a value of 1.0 g. Any further increases in the amount of CNT added to the mixture resulted in a linear rise in peak current but with a lower slope. Increasing the aniline monomer weight had the effect of increasing the peak current. But, when the aniline monomer weight reached or exceeded 0.70 g, a constant peak current was observed. Based on these results, 1.0 g of CNT and 0.70 g of aniline monomer were used in all experiments.

Electrode preparation

A composite electrode was prepared by carefully homogenizing (using slow rubbing) a mixture of 0.35 g graphite powder, 0.050 g PANi–MWCNTs, precipitated with 7:1 weight ratio, and 2 drops of paraffin oil, for 15 min. The resulting paste was then packed into a polyethylene tube. The electrode surface (0.048 cm^2) was renewed by extrusion of a approximately 0.5 mm carbon paste from the holder and smoothed with filter paper.

RESULTS AND DISCUSSION

Voltammetric behavior of the PANi–MWCNTs electrode

Cyclic voltammetry was used for the study of PANi–MWCNTs modified chemically with polymerized aniline. The cyclic voltammograms obtained for both PANi and PANi–MWCNT composite electrodes at a scan rate of 50 mV s^{-1} in the potential range -0.20 to 1.0 V are shown in Fig. 1. Three identifiable anodic peaks with cathodic counter parts are observed for the PANi–MWCNT composite electrode but not for the PANi composite electrode. Here, it is also important to take note of the role played by the CNT in the PANi composite.

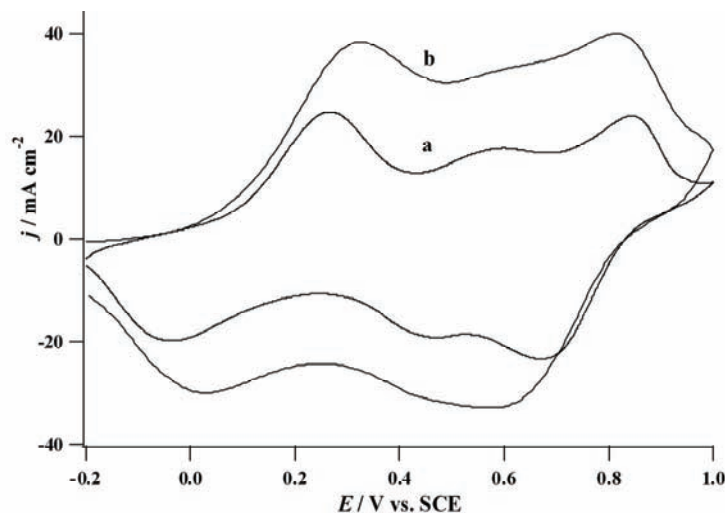


Fig. 1. Cyclic voltammograms of a) PANi–MWCNTs and b) PANi composite electrodes in 0.50 M HCl at a scan rate of 50 mV s^{-1} .

As can be seen in Fig. 1, the cyclic voltammograms have a defined peak at approximately 200 mV , corresponding to the formation of radical cations, a second peak at 500 mV , corresponding to the oxidation of benzoquinone (a hydrolysis product), and a third peak at 700 mV , corresponding to the oxidation of radical cations to diamine and formation of quinoid. Surface coverage (Γ) could be evaluated from the area under the first anodic peak of the cyclic voltammograms for the PANi–MWCNT composite electrode. The surface coverage for PANi–MWCNTs was calculated according to Eq. (1):²⁵

$$\Gamma = Q/nFA \quad (1)$$

where Q is the charge obtained by integration of the current vs. time for the first anodic peak, A is the surface area of the anodic peak, and n is the number of electrons transferred. Using this equation, the surface coverage, $\Gamma = 2.369 \times 10^{-8} \text{ mol cm}^{-2}$, was calculated.

The peak-to-peak separations ($\Delta E = E_{pa} - E_{pc}$) were calculated for a PANi/MWCNT composite electrode using scan rates of up to 50 mV s^{-1} in the presence of HCl as the supporting electrolyte. At higher scan rates, ΔE increased, indicating a limitation arising from the kinetics of the charge transfer.

Laviron derived general expressions for the linear potential sweep voltammetric response for the case of surface-confined electroactive species.²³ According to Laviron, the standard rate constant (k_s) in 0.50 M HCl as the supporting electrolyte was calculated to be $6.9 \times 10^{-8} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ when a scan rate of 3.0 mV s^{-1} was applied and using values for $\Delta E_p > 200/n$ (mV) with $\alpha = 0.42$.

Morphology of the PANi-MWCNTs composite

PANi was obtained by polymerization in the presence of 15 mass % c-MWCNTs. The scanning electron microscopy (SEM) technique was used for studying the morphology of the MWCNTs coated with PANi and the results are shown in Fig. 2. SEM Revealed a uniform deposition of PANi onto the MWCNTs, whereby the diameter of the PANi-coated MWCNTs was estimated to be in the range 80–120 nm.

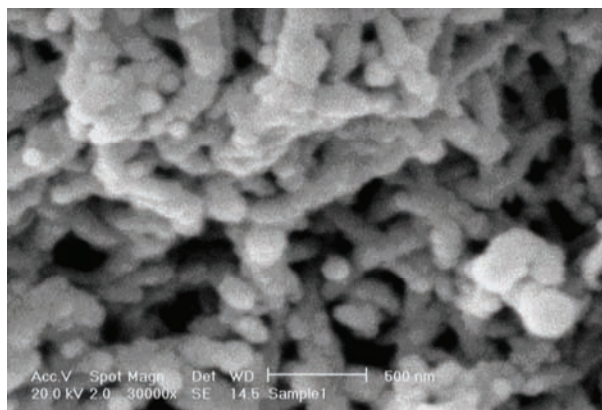


Fig. 2. SEM Image of a PANi/MWCNT nanocomposite.

FTIR Results

The FTIR spectra obtained for MWCNTs and c-MWCNTs are presented in Fig. 3. The peaks at 1190 and 1720 cm^{-1} correspond to the stretching modes of the carboxylic acid groups, and thus confirm the formation of carboxylic acid groups on the walls of the MWCNTs at defect sites.

Thermal stability of the electrodes

The thermal stability of the electrode was verified by subjecting it to different temperatures (15, 25, 35 and $45 \text{ }^\circ\text{C}$) for 2 h under dry conditions. The shapes of voltammetric curves were maintained and only a 6.5 % decrease of initial peak current was observed at the highest temperature ($45 \text{ }^\circ\text{C}$). The good thermal sta-

bility of the PANi–MWCNTs composite may be attributed to the stability of PANi itself and the protective effect of PANi against desorption of MWCNTs from the composite.

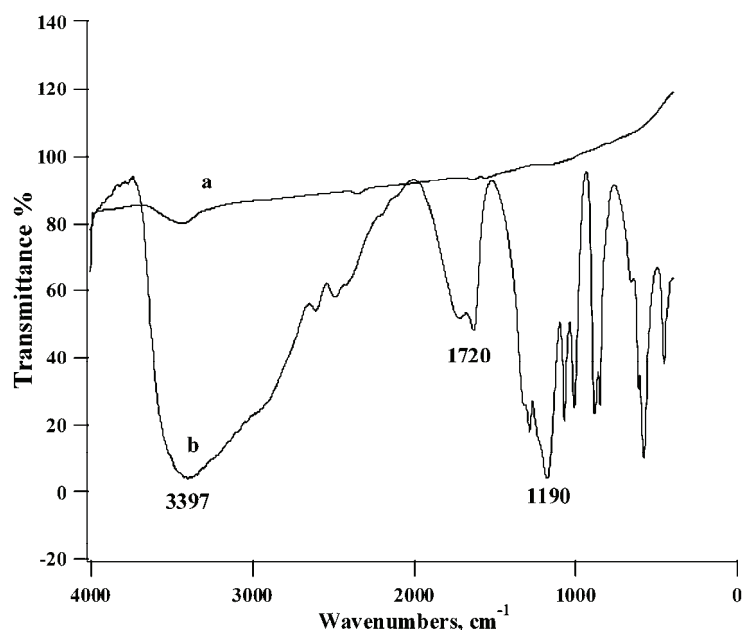


Fig. 3. The FTIR spectra of a) MWCNTs and b) c-MWCNTs.

Response time, reversibility and reproducibility of the electrode

The electrode response time was less than 20 s. The inset of Fig. 4 shows the calibration graph. The long-term response of the electrode for DA determination under hydrodynamic conditions was evaluated at 30-min intervals. The experimental results show that there was no appreciable change in the response for DA determination over time suggesting that the electrode remains stable even under stirring and, hence, may be used as a sensor for the determination of DA in flow systems. The response of the modified electrode remained reproducible and stable for almost one month without the need for its reactivation or remodification.

To characterize the reproducibility of the preparation of the PANi–MWCNTs composite, repetitive preparations of PANi–MWCNTs composite were made and tested. The relative standard deviation in the accompanying electrode signal for 5 successive preparations on different days was 6.8 %, indicating that successive preparations of PANi–MWCNTs yields a reproducible electrode activity. The modified electrode also exhibited high stability. For example, only a 5.4 % drop in the electrode signal from its initial response was observed when the electrode was used successively during a 1-day period.

Reproducibility of the PANi–MWCNTs composite modified electrodes stored in air or phosphate buffer at room temperature were investigated by measuring their current responses under both storage conditions at weekly intervals. The experimental results show that during a 4-week storage period of electrodes in a 0.10 M phosphate buffer solution and in air, the response currents of the PANi/MWCNTs composite modified electrodes decreased gradually to 12 and 19 % of their initial values, respectively.

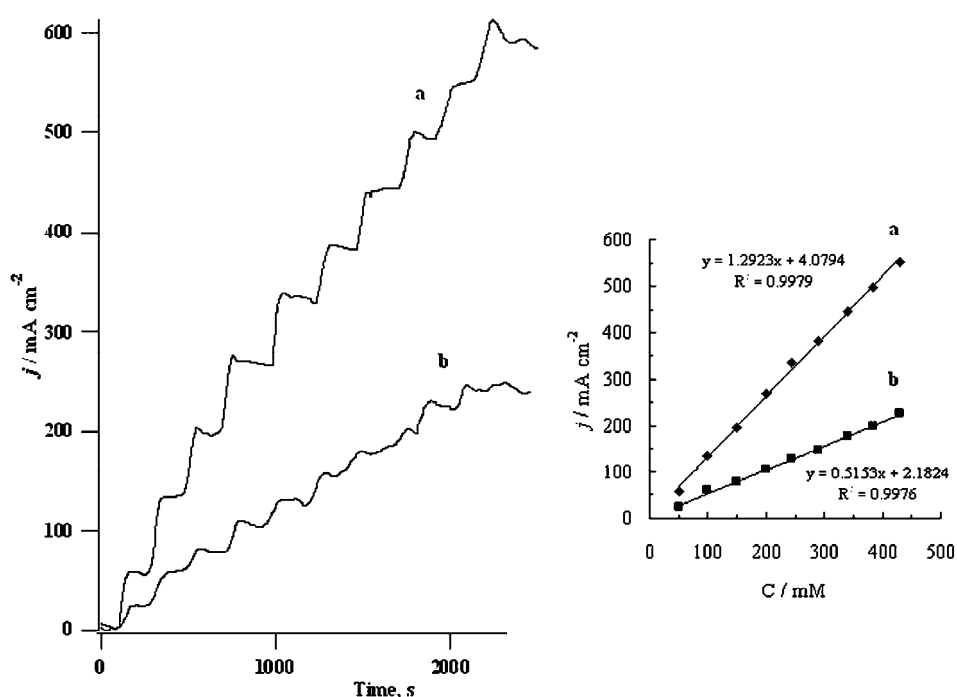


Fig. 4. Amperometric current response curves resulting from experiments with a) a PANi–MWCNTs nanocomposite electrode and b) a PANi carbon paste electrode. The points on the curves follow successive additions of 50 μM DA in 0.10 M phosphate buffer at pH 7.0 and 0.70 V (the corresponding calibration curves are given in the inset).

Electrocatalysis of dopamine oxidation

Amperometric studies. Typical current–time plots for the PANi–MWCNT and PANi composites upon successive addition of 50 μM dopamine under stirred conditions at 0.70 V are illustrated in Fig. 4. The PANi–MWCNT composites attained 95 % of the steady-state current within a reaction time of 15 s. The calibration curve of dopamine at the PANi–MWCNT composite electrode is shown in Fig. 4 (inset). The composite electrode exhibited a linear response to DA in the

range from 50.0 to 385 μM with a correlation coefficient of 0.9979. The electrode was found to have a low detection limit of 38 μM .

Cyclic voltammetry studies. Cyclic voltammetry was performed to study the electrocatalytic behavior of PANi–MWCNTs toward the oxidation of DA in 0.10 M phosphate buffer (pH 7.0) and to compare to different composite electrodes. The cyclic voltammograms of PANi–MWCNTs, PANi, MWCNTs and carbon paste electrodes in the presence of 3.7 mM of DA are shown in Fig. 5. Experiments with PANi–MWCNTs resulted in pronounced electrocatalytic activity for the oxidation of DA in comparison to those using a PANi electrode alone, MWCNT or a carbon paste electrodes (Fig. 5). The peak current enhancement for DA oxidation (2.56 mA cm^{-2}) at a low oxidation potential ($E_{\text{pa}} = 269 \text{ mV vs. SCE}$) is clearly observed. The enhanced current peak and the negative shift (see Table I) in the oxidation overvoltage for DA oxidation indicates enhanced electrocatalytic activity associated with the PANi–MWCNTs electrode. The observed shift in the oxidation overvoltage for DA oxidation may be related to kinetic and transport effects of DA at the PANi–MWCNT interface. A substantial increase in the electron transfer rate at an electrode may promote enhancement of the oxidation of DA.

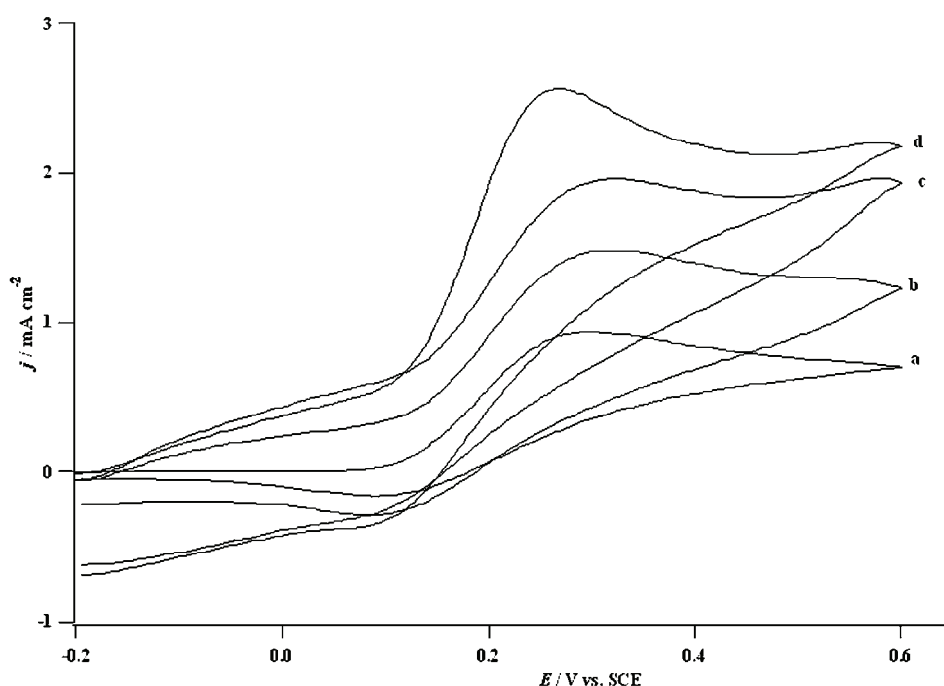


Fig. 5. Cyclic voltammograms of a) a carbon paste electrode, b) PANi, c) MWCNTs and d) PANi–MWCNTs in the presence of 3.7 mM DA.

Table I. Oxidation potential of DA using different electrodes

Composite electrode	DA oxidation potential, mV vs. SCE
Carbon paste	313
MWCNTs 308	
PANi 300	
PANi-MWCNTs 269	

Chronoamperometric studies. Chronoamperometry was used to calculate the diffusion coefficient of DA. The well-defined chronoamperograms acquired for PANi-MWCNT modified electrodes at applied potential steps of 0.50 and 0.0 V for the forward and backward chronoamperometry, respectively, both in the absence and presence of 1.66 and 2.85 mM DA, are shown in Fig. 6. The forward and backward potential step chronoamperometry of the composite electrode in the absence of DA shows very symmetrical chronoamperograms with an equal charge consumed for the oxidation and reduction of the surface-confined PANi-MWCNT sites. For electro-active materials with a diffusion coefficient D , the current corresponding to the electrochemical reaction (under diffusion control) is described by the Cottrell Law:²⁶

$$I = nFAD^{1/2}c(\pi t)^{-1/2} \quad (2)$$

where D and c are the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) and bulk concentration (mol cm^{-3}), respectively. Thus, a plot of I vs. $t^{-1/2}$ should be linear and from its slope, the value of D can be obtained.

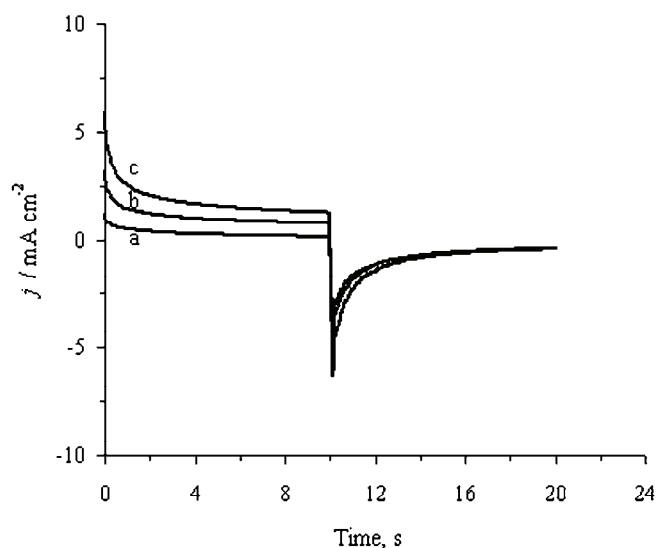


Fig. 6. Chronoamperograms acquired with a PANi-MWCNT composite electrode in 0.10 M phosphate buffer, pH 7.0, in a) the absence, b) presence of 1.66 mM DA and c) presence of 2.85 mM DA.

The mean value of D was found to be $(7.98 \pm 0.8) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (for 5 repetitions and at the 95 % confidence limit). Chronoamperometry also can be used to evaluate the kinetics of a reaction. At intermediate times (0.1–5 s in the present work), the catalytic current (I_{cat}) is dominated by the rate of electron cross-exchange between the PANi–MWCNT redox sites and DA. The rate constant in this time limit was determined according to Eq. (3) as described in the literature:²⁷

$$I_{\text{cat}}/I_{\text{L}} = \gamma^{1/2} \pi^{1/2} = \pi^{1/2} k c_0 t \quad (3)$$

where k , c_0 , t , I_{cat} and I_{L} are the catalytic rate constant ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), analyte concentration (mol dm^{-3}), time elapsed (s), and current of the PANi–MWCNT composite electrodes in the presence and absence of DA, respectively. From the slope of the $I_{\text{cat}}/I_{\text{L}}$ vs. $t^{1/2}$ plot, the value of k for a given concentration of DA can be calculated. According to the experimental data, the value of k was found to be $(8.33 \pm 0.072) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (for 6 repetitions and at the 95 % confidence limit).

Study of interferences

The possible interferences from substances such as ascorbic acid, AA, and uric acid, UA, were evaluated using the Differential Pulse Voltammetry (DPV) technique. Oxidation of DA on a PANi–MWCNTs electrode in 0.10 M phosphate buffer solution (pH 6.0) occurred at 0.10 V vs. SCE. The oxidation of ascorbic acid at the same concentration and pH resulted in a peak at 0.18 V vs. SCE in 0.10 M phosphate buffer (pH 6.0). Under identical solution conditions (0.10 M phosphate buffer, pH 6.0), uric acid produced a peak at 0.32 V vs. SCE. According to the experimental results, the amount of DA can be determined in the presence of ascorbic acid or uric acid by adjusting the pH.

According to the experimental results obtained using the PANi–MWCNTs electrode, the peak separation of DA vs. ascorbic acid realized by the DPV technique is less than 0.10 V. A similar investigation with DA and uric acid identified a peak separation of 0.22 V. Typical amounts in grams of DA determined by the DPV method in the presence of ascorbic acid or uric acid are shown in Fig. 7, from which it can be seen that successive additions of uric acid or ascorbic acid causes an increase in the peak current. From this, it can be concluded that the determination of the amount of DA in the presence of ascorbic acid or uric acid is possible using this electrode.

Analytical application to real samples

The applicability of the modified electrode was evaluated by measuring the concentration of DA in pharmaceutical injection samples. The injection samples were diluted with phosphate buffer solution (pH 6.0) without any further treatment. The DPVs for a DA sample in phosphate buffer solution were recorded.

An oxidation peak at 0.10 V was observed, which was assigned to the oxidation of DA. To check that the observed oxidation peak at 0.1 V did in fact originate from DA, a secondary experiment was performed in which the sample was spiked with specific amounts of a DA standard solution and the corresponding DPVs were recorded. The obvious increase in the peak current after addition of DA to the injection sample is a clear sign that the observed peak corresponded to the oxidation of DA.

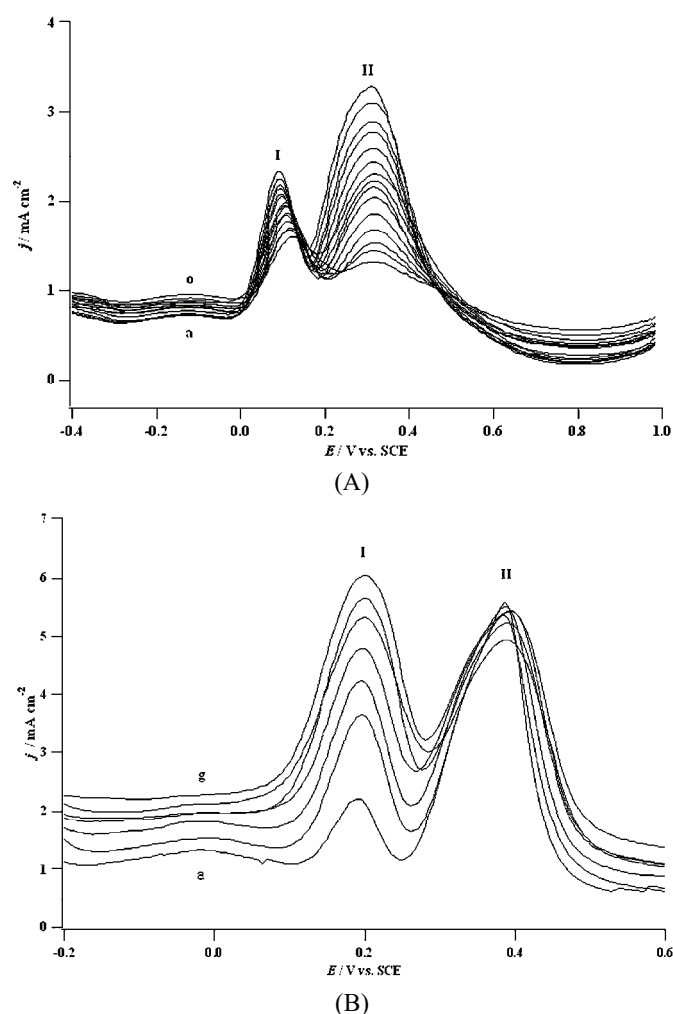


Fig. 7. DPV Voltammograms of a PANi-MWCNT electrode for A) peak I – 50 μM of DA and peak II – different concentrations of UA (a–n: 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75 and 80 μM) and B) peak I – different concentrations of DA (a–g: 40, 50, 60, 70, 80, 100 and 120 μM) and peak II – 50 μM of AA in phosphate buffer (pH 6.0).

The relative recoveries of DA for some injection samples were investigated. For this purpose, an analytical curve was constructed using hydrodynamic voltammetry. Thus, a voltage 0.30 V vs. SCE was applied to the electrode and the samples were analyzed using a calibration plot. In addition, a definite quantity of standard DA solution was added to the corresponding injection samples in order to test for DA recovery. Typical results are shown in Table II. The recovery was acceptable, showing that the proposed methods could be efficiently employed for the quantification of DA in pharmaceutical injection samples. The recoveries of DA observed after spiking pharmaceutical injection samples ($n = 3$) with a fixed quantity of DA solution varied from 97 to 99 % (Table II) using the proposed sensor.

Table II. Results of the determination of DA in pharmaceutical injection samples (DA spiking, $50.0 \times 10^{-5} \text{ mol dm}^{-3}$)

Sample	DA Found, $10^{-5} \text{ mol dm}^{-3}$	Recovery, %
1	49.5	99
2	48.5	97
3	48.5	97

CONCLUSIONS

The preparation of PANi–MWCNTs and their employment for the measurement of the electrocatalytic activity of DA have been described. The PANi–MWCNT nanocomposites were prepared using an *in situ* chemical polymerization reaction between MWCNTs and PANi monomer. The presence of functionalized MWCNT composites caused an increase in the DA oxidation current. The morphology of the PANi–MWCNTs was studied by the SEM technique and FTIR spectroscopy confirmed the incorporation of carboxylic acid groups into the MWCNTs.

ИЗВОД

НАНОКОМПОЗИТ ПОЛИАНИЛИНА И УГЉЕНИЧНИХ НАНОЦЕВИ КАО ДОПАМИНСКИ СЕНЗОР

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Композитни материјал полианилина и вишеслојних угљеничних наночевеи (PANi–MWCNT) је синтетисан методом *in situ* хемијске оксидативне полимеризације. Наночестице полианилина су синтетисане хемијским путем коришћењем анилина као мономера и амонијум-пероксодисулфата као оксидационог средства. Наноконтролнати материјал је припремљен коришћењем функционализованих вишеслојних угљеничних наночевеи и наночестица полианилина у виду угљеничне пасте. Композит PANi–MWCNT је карактерисан скенирајућом електронском микроскопијом, док је његово електрохемијско понашање у киселом раствору (HCl) испитано цикличном волтаметријом. Електрода направљена од компо-

зита PANi-MWCNT је коришћена за испитивање допамина као електроактивне врсте. Резултати цикличне волтаметрије су показали да вишеслојне угљеничне наноцеви значајно побољшавају електрокаталитичку активност за оксидацију допамина. Кинетика ове реакције је испитивана методом хроноамперометрије. Одређена је средња вредност коефицијента дифузије ($(7,98 \pm 0,8) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) и константа брзине каталитичке оксидације допамина ($(8,33 \pm 0,072) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).

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