

Voltammetric Determination of Gabapentin by a Carbon Ceramic Electrode Modified with Multiwalled Carbon Nanotubes and Nickel-Catechol Complex

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A técnica sol-gel foi usada na fabricação de um eletrodo cerâmico de carbono (CCE) renovável com complexo níquel-catecol (Ni-CA). O complexo foi depositado na superfície de nanotubos de carbono de parede múltipla-CCE por potencial cíclico na faixa de 0,0-0,8 V (vs. eletrodo saturado de calomelano, SCE). Ni-CA mostrou ter atividade catalítica sobre a reação redox de gabapentina. Observou-se uma relação linear da corrente de pico anódico com a concentração de gabapentina na faixa de 1,25-63,23 $\mu\text{mol L}^{-1}$ com um limite de detecção de 0,5 $\mu\text{mol L}^{-1}$. A resposta do eletrodo com respeito à gabapentina era bem reproduzível e observou-se estabilidade a longo prazo do eletrodo (acima de 2 meses). O eletrodo foi aplicado com sucesso à determinação de gabapentina em preparações farmacêuticas.

Sol-gel technique was used for the fabrication of a renewable carbon ceramic electrode (CCE) modified with nickel-catechol complex (Ni-CA). The complex was deposited on the surface of a multiwalled carbon nanotubes-CCE by potential cycling in the range of 0.0-0.8 V (vs. saturated calomel electrode, SCE). Ni-CA showed electrocatalytic activity towards the redox reaction of gabapentin. A linear relationship of anodic peak current with gabapentin concentration was observed in a range of 1.25-63.23 $\mu\text{mol L}^{-1}$ with a limit of detection of 0.5 $\mu\text{mol L}^{-1}$. The electrode response towards gabapentin was quite reproducible and a long-term stability of the electrode (more than 2 months) was observed. The electrode was successfully applied to the determination of gabapentin in pharmaceutical preparations.

Keywords: carbon ceramic electrode, gabapentin, nickel, catechol, electrocatalysis

Introduction

Gabapentin (GP), 1-(aminomethyl)cyclohexane acetic acid, is an antiepileptic drug which is also effective in the prevention of frequent migraine headaches, neuropathic pain, and nystagmus. It is a cyclic analogue of gamma-aminobutyric acid (GABA) which may alter GABA transmission in the central nervous system.^{1,2} The lipophilic cyclohexane ring in its structure allows GP, unlike GABA, to cross the blood-brain barrier. GP increases the rate of synthesis and accumulation of GABA, decreases the release of monoamines (dopamine, norepinephrine, and serotonin), and weakly inhibits GABA-transaminase, an enzyme which degrades GABA into other amino acids.³

Due to the absence of chromophores and fluorophores in GP, derivatization is a part of the electrophoretic and chromatographic[20] assays for the drug analysis. For example, in electrophoretic methods, derivatization of GP

with fluorescamine,⁴ and 6-carboxyfluorescein succinimidyl ester⁵ was used to provide chromophores for UV absorption and fluorescence detection. In chromatographic methods, reagents such as 9-fluorenylmethyl chloroformate,⁶ 4-fluoro-7-nitrobenzofurazan,⁷ and 1-fluoro-2,4-dinitrobenzene⁸ were used for the determination of GP with fluorescence detectors.

Electrochemical methods, on the other hand, have been proven to be very sensitive to the determination of drugs and related molecules. The advance in electrochemical techniques in the field of analysis of drugs is due to the simplicity, low cost and relatively short analysis time when compared to electrophoretic and chromatographic techniques. Moreover, the use of chemically modified electrodes in electrochemical methods is widely reported for sensitive and selective determination of various pharmaceuticals.^{9,10}

Sol-gel electrochemistry has rapidly developed over the last years and has become an area of active research.¹¹ The ability to form inorganic-organic hybrids and tailoring

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thin films make it attractive for the field of chemically modified electrodes.^{12,13} Carbon-ceramic composite electrodes (CCEs) are comprised of a dispersion of carbon powder that is held together by a ceramic binder. The ceramic material is produced from the low temperature sol-gel process which involves the hydrolysis of an alkoxide precursor, followed by condensation of the hydroxylated monomer.^{11,14}

The composite electrode benefits from the mechanical robustness of the silicate backbone, resistance to air oxidation and to hydrolysis under extreme pH conditions. Electron conductivity through the interconnected carbon grains and the ability to manipulate the physicochemical characteristics of the matrix by incorporation of suitable monomer precursors or sol-gel dopants are other advantages of CCEs.

Gavalas *et al.* reported the fabrication of carbon nanotube (CNT) composite electrodes based on the sol-gel technique.¹⁵ The composite carries with it the advantages of both CNTs^{16,17} and CCEs. Thereafter, various procedures were employed for the fabrication of CCEs modified with CNTs (single- and multiwalled) and they have been used in sensing of important organic and inorganic compounds.¹⁸⁻²²

Moreover, CCEs can be appropriately modified by metallic redox mediators.²³⁻²⁵ Several modified CCEs were recently used for the determination of pharmaceutical compounds.^{18,21,26}

GP is not electroactive at the surface of most unmodified electrodes; the only report is on gold electrode.²⁷ Chemically modified electrodes such as nanotubes of nickel oxide-modified carbon paste electrode²⁸ and silver nanoparticle modified multiwalled carbon nanotubes (MWCNTs) paste electrode²⁹ were used for the voltammetric determination of GP, through an electrocatalytic mechanism.

In this work, Ni-catechol complex (Ni-CA) was deposited on the surface of a MWCNT-CCE electrode and used in the electrocatalytic determination of GP. Carbon paste electrode that has been used in the determination of GP²⁸ is nonporous, and therefore only its outermost surface is wetted by the electrolyte and accessible to dissolved substrates. In contrast, CCE has a porous structure, which is not clogged by the mechanical polishing step, due to the brittleness of the inorganic matrix, and is highly resistant to plastic deformations. Thus, highly reproducible responses were observed by using CCEs instead of carbon paste electrodes.³⁰

Moreover, the resistance of CCE to extreme pH conditions (in this work, pH 13), and the advantages of MWCNTs, such as improvement in the rate of electron transfer and enlargement of surface area were considered in the present work.

Experimental

Reagents and solutions

Methyltriethoxysilane (MTEOS) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were from Merck. MWCNTs (20-50 nm o.d., purity > 95%) and graphite powder were purchased from Aldrich. GP powder was from Bakhtar Bioshimi Pharmaceutical Company (Kermanshah, Iran). All other chemicals were of analytical grade and used without further purification. All solutions were freshly prepared using doubly distilled water.

Apparatus

Electrochemical measurements were performed with μ -Autolab type III potentiostat/galvanostat instrument. Data acquisition was performed using software NOVA 1.8. A three-electrode system consisting of a saturated calomel electrode (SCE) as the reference, a platinum wire as the counter electrode, and a modified MWCNT-CCE as working electrode was employed for the electrochemical measurements. All experiments were conducted at room temperature. A pHmeter (Jenway, Model 140) with a combined glass electrode was used to check the pH levels of the solutions.

Preparation of Ni-CA/MWCNT-CCE

MWCNT-CCE was prepared according to the procedure described by Lev and co-workers.¹⁴ Briefly, a mixture of MTEOS (0.2 mL), methanol (0.6 mL) and hydrochloric acid (20 μL , 11 mol L^{-1}) was magnetically stirred to ensure uniform mixing, after which graphite powder (1.0 g) and MWCNTs (0.01 g) were added and the mixture was shaken for 5 min. The mixture was packed into a Teflon tube (2 mm i.d.), and dried at room temperature for 48 h. The prepared MWCNT-CCE was polished with polishing paper to remove any extra composite material.

Ni(II)-catechol complex (Ni-CA) was deposited on the electrode surface by immersing MWCNT-CCE in NaOH solution (0.1 mol L^{-1}) containing a 2:1 mixture of CA (0.36 mmol L^{-1}) and $\text{Ni}(\text{NO}_3)_2$ (0.18 mmol L^{-1}), and applying the potential ramp between 0 and 100 mV (*vs.* SCE) with a scan rate of 50 mV s^{-1} in a cyclic voltammetry regime.³¹⁻³³

Determination of GP in tablets

A homogenized powder was prepared from ten accurately weighed tablets (100 mg tablet⁻¹). A proper

portion of the powder equivalent to 0.021 g GP was added to HCl solution (2 mL, 0.01 mol L⁻¹). Dissolution of the drug was assisted by means of ultrasonication. After filtration on a filter paper, the solution was made up to the mark with distilled water in a 50 mL volumetric flask. A 10 mL portion of this solution was transferred into a 25 mL volumetric flask and diluted with distilled water. The GP content was determined by linear sweep voltammetry (LSV) using the modified electrode.

Results and Discussion

Electrochemical behavior of Ni-CA/MWCNT-CCE

Cyclic voltammograms of separate solutions of Ni, CA, and Ni-CA in NaOH (0.1 mol L⁻¹) on MWCNT-CCE are compared in Figure 1. In the case of Ni(NO₃)₂ solution (curve a), well-defined anodic and cathodic peak currents of Ni(II)/Ni(III) were observed on a large background current. The corresponding half-reaction is:

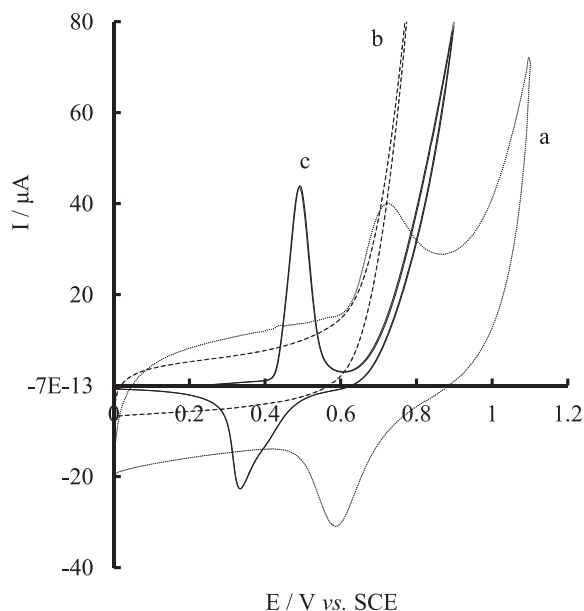


Figure 1. Cyclic voltammograms of MWCNT-CCE in a solution containing: (a) Ni(NO₃)₂; (b) catechol; (c) Ni + catechol. [NaOH] = 0.1 mol L⁻¹.

The formal potential, $E^{\circ'}$, was calculated ($= (E_{pa} + E_{pc})/2$) as about 0.65 V. The peak separation ($\Delta E_p = E_{pa} - E_{pc}$) of 0.16 V shows the quasi-reversible nature of the electron transfer.

CA showed no distinguishable peak (curve b) because, at highly alkaline media, CA undergoes hydrolysis and converts to quinone in solution. In a mixture of Ni(II) and CA (curve c), however, a well-defined pair of anodic

and cathodic peaks were observed at lower potentials ($E^{\circ'} = 0.41$ V) with very low background current. Indeed, Ni-CA complex is formed between the oxidized form of CA (*o*-quinone) and nickel ions (Figure 2), which is more readily adsorbed at the electrode surface,³⁴ and a large negative shift in oxidation potential results. The presence of MWCNTs in CCE provided a larger surface area for Ni-CA to be deposited, and accelerated electron transfer rate between Ni-CA and the substrate electrode.¹⁹

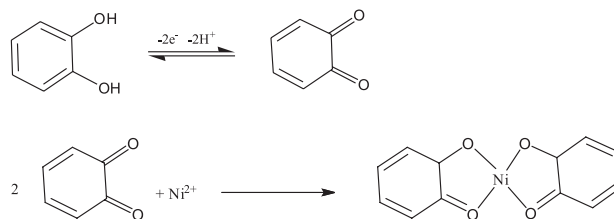


Figure 2. Mechanism of the formation of the deposited Ni-CA complex.

Consecutive potential cycling on MWCNT-CCE (16 cycles) showed increasing anodic and cathodic currents in a 2:1 mixture of CA and Ni(NO₃)₂ in alkaline solution (0.1 mol L⁻¹ NaOH). Figure 3 shows the result of repeated cyclic voltammograms in the range of 0.0-0.8 V (vs. SCE) with a scan rate of 50 mV s⁻¹. Increasing of anodic and cathodic currents with the number of potential cycles confirms the electrodeposition of the redox species (Ni-CA) on MWCNT-CCE. The ratio of cathodic peak current (I_{pc}) to anodic one (I_{pa}) was about unity, which showed the stability of the oxidation product at the electrode surface.

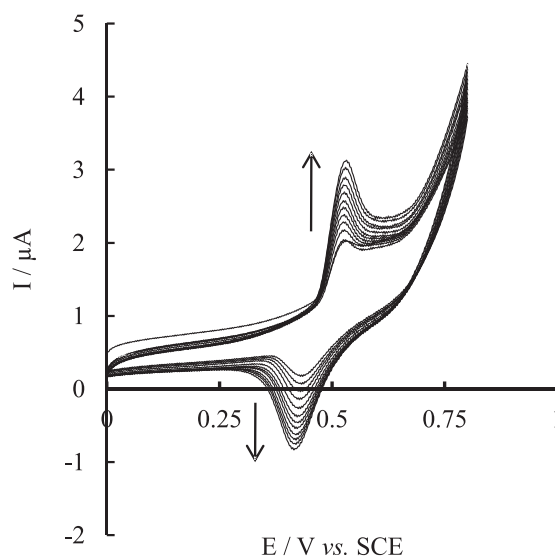


Figure 3. Consecutive cyclic voltammograms on MWCNT/CCE in NaOH (0.1 mol L⁻¹) containing CA (0.36 mmol L⁻¹) and Ni(NO₃)₂ (0.18 mmol L⁻¹). Scan rate: 50 mV s⁻¹.

Effect of pH on redox behavior of Ni-CA/MWCNT-CCE

The influence of pH was examined on the voltammetric behavior of Ni-CA/MWCNT-CCE in the pH range from 10 to 13, and the results are shown in Figure 4. As is shown, by increasing the pH, enhancement of anodic and cathodic peak currents was observed and the formal potential E° ($= (E_{pa} + E_{pc}) / 2$) of the redox couple shifted to less positive potentials (Figure 4 inset), suggesting that OH^- participated in the redox process of the modified electrode. The large slope (which was reported in literature, previously)^{35,36} could not be related to the ratio of the number of H^+ and electrons in the electron transfer mechanism, due to the quasi-reversible behavior of Ni(II)/Ni(III) redox couple. The peak disappeared at $\text{pH} \leq 9$ as was reported earlier for the redox couple.³⁶

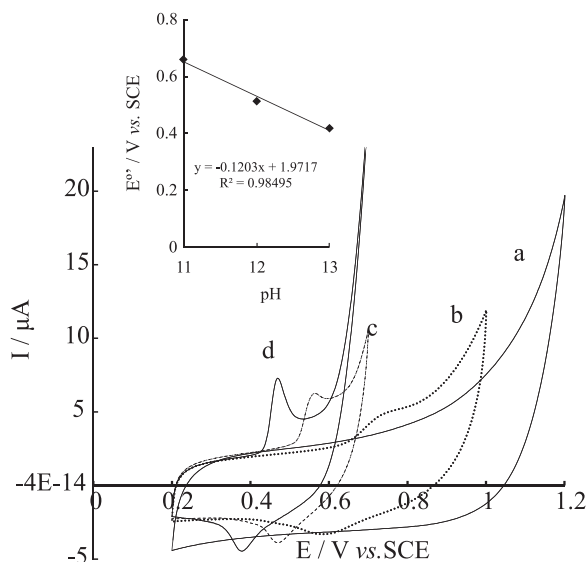


Figure 4. Cyclic voltammograms of Ni-CA/MWCNT-CCE at different pH: (a) 10; (b) 11; (c) 12; (d) 13. Inset: plot of formal potential against pH.

Voltammetric behavior of Ni-CA/MWCNT-CCE in the presence of GP

Due to the strong complex formation between GP and Ni(II),³⁷ the effect of the presence of the drug was examined on the response of Ni-CA/MWCNT-CCE. The electrocatalytic properties of nanotubes of nickel oxides (dispersed in a carbon paste electrode) on the electro-oxidation of GP was previously reported.²⁸

As is shown in Figure 5, in the presence of GP ($26.7 \mu\text{mol L}^{-1}$), both anodic and cathodic peaks increased. The increase of oxidation current was attributed to the production of Ni(II) through the reaction between Ni(III) and GP:

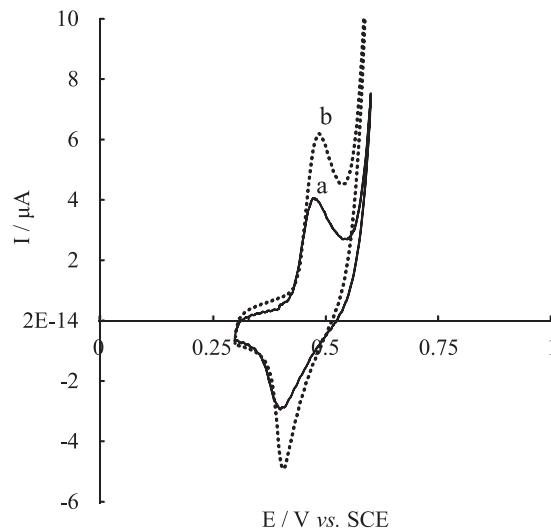


Figure 5. Cyclic voltammograms of Ni-CA/MWCNT-CCE in (a) NaOH (0.1 mol L^{-1}); (b) NaOH + GP ($26.7 \mu\text{mol L}^{-1}$). Scan rate: 20 mV s^{-1} .

However, the cathodic current increased as well. This behavior was observed at the surface of nickel-modified electrodes for the electrocatalytic determination of glucose³⁸ and l-histidine.³⁹ Because Ni(II)/Ni(III) redox couple serves as both an electronical medium (enhancing cathodic and anodic currents simultaneously) and a catalyst, the electrochemical behavior is different from typical mediated catalytic oxidation in which the cathodic peak current decreases.

Effect of scan rate on Ni-CA/MWCNT-CCE in the presence of GP

The influence of scan rate was investigated in the range of $10\text{--}100 \text{ mV s}^{-1}$ on the electrochemical behavior of Ni-CA/MWCNT-CCE in the presence of GP. Both cathodic and anodic currents increased with scan rate (Figure 6a). Linear increase of peak current with scan rate (Figure 6b) indicates an adsorptive redox process, which may be due to the tendency of GP to interact with nickel ions at the electrode surface.³⁶ The plot of $\log(I_{pa})$ against $\log(v)$ was linear (Figure 6c) with a slope of about 0.83, which shows the large contribution of adsorption of GP to the current flow; in the case of diffusion currents, the slope approaches 0.5.⁴⁰

Effect of accumulation time

Due to the importance of GP adsorption, the effect of accumulation time (t_{acc}) was investigated on current response of the modified electrode, as depicted in Figure 7. The peak current increased with t_{acc} up to 10 min, beyond which it leveled off due to the saturation of the active

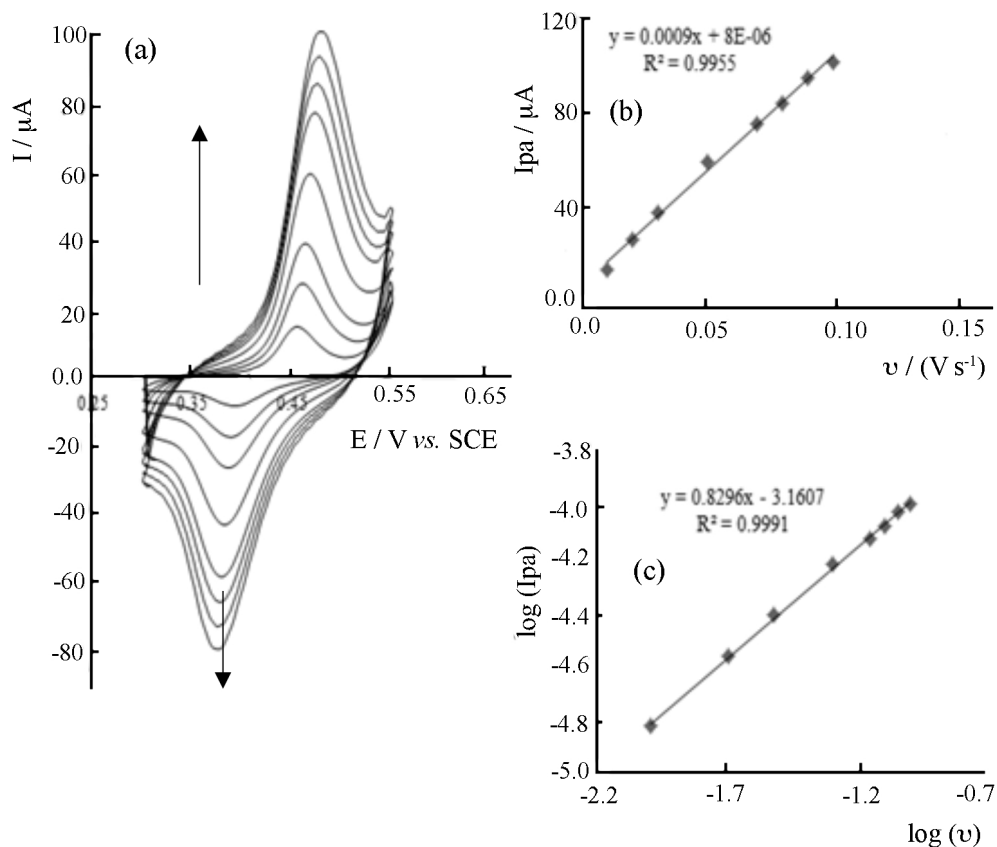


Figure 6. (a) Cyclic voltammetry on Ni-CA/MWCNT-CCE at different scan rates (0.01-0.1 V s⁻¹) in the presence of GP (7.44 μmol L⁻¹) in NaOH (0.1 mol L⁻¹); (b) plot of anodic peak current against scan rate; (c) plot of log(Ipa) against log(v).

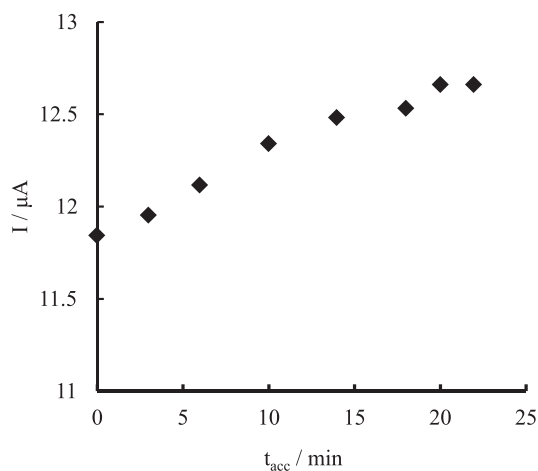


Figure 7. Effect of accumulation time (t_{acc}) on anodic peak current of Ni-CA/MWCNT-CCE in the presence of GP.

surface of the electrode. Therefore, the sample solutions were equilibrated with the electrode surface for 10 min before each measurement.

Linear range and limit of detection

Linear sweep voltammetry (LSV) was applied to the determination of GP on Ni-CA/MWCNT-CCE

(Figure 8). In the absence of GP, the oxidation peak current is due to Ni(II)/Ni(III) redox couple at the surface of Ni-CA/MWCNT-CCE. In the presence of GP, peak current was increased linearly with GP concentration in the range of 1.25-63.23 μmol L⁻¹, with the regression line: $I_p / \mu A = 0.072 [GP] / \mu mol L^{-1} + 4 \times 10^{-6}$, with $R^2 = 0.995$. The limit of detection (LOD) was calculated by using the equation: $Y_{LOD} = Y_B + 3S_B$,⁴¹ in which Y_{LOD} is the peak current at LOD, Y_B is the average current for blank solution (= intercept of the calibration curve), and S_B is the standard deviation of replicate measurements of the blank measurements. A value of 0.5 μmol L⁻¹ was calculated for LOD.

Repeatability and stability of Ni-CA/MWCNT-CCE

For six successive determinations of GP (26.7 μmol L⁻¹) under optimum conditions, the anodic current was nearly constant (relative standard deviation, RSD% = 0.67%). The excellent repeatability (intra-day) of the results is one of the advantages of CCEs, because, unlike carbon paste electrodes, the porous structure of the electrode is not clogged by the mechanical polishing step, and it is highly resistant to plastic deformations. The inter-day repeatability of the method was examined by using

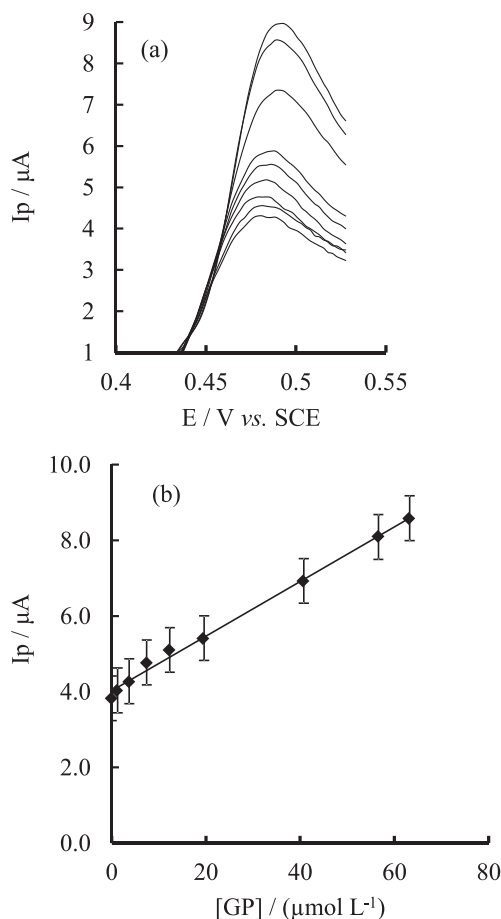


Figure 8. (a) LSVs of Ni-CA/MWCNT-CCE for GP (0-63.23 $\mu\text{mol L}^{-1}$) in NaOH (0.1 mol L^{-1}); scan rate = 0.02 V s^{-1} ; (b) calibration curve.

Ni-CA/MWCNT-CCE in the voltammetric determination of GP (25 $\mu\text{mol L}^{-1}$) in four different days. A value of $\text{RSD}\% = 2.94\%$ was obtained, which shows the stability of the electrode response during using, and storage in a long time period.

The electrode showed excellent stability over a period of 2 months (the peak current for GP was changed to 90% of its initial response after this period), which is partly due to the mechanical robustness of CCEs and resistance to extreme pH conditions. The electrode was shelf-stored when it was not used.

Comparison of the analytical figures of Ni-CA/MWCNT-CCE for GP determination with similar reports is shown in Table 1. The linear range and LOD of the proposed method is comparable with some of the previous reports. The sensitivity was improved compared to nickel-oxide nanotube carbon paste electrode,²⁸ which may be due to the larger amount of Ni(II)/Ni(III) redox couple at the surface of Ni-CA/MWCNT-CCE. The presence of MWCNTs and highly porous structure of CCE provide a larger surface area for Ni-CA deposition.

Interference studies

The influence of various inorganic ions and organic compounds on the determination of GP (20 $\mu\text{mol L}^{-1}$) was studied at optimum conditions. The results showed that in the presence of 1000-fold of Ca^{2+} , Mg^{2+} , Br^- , NH_4^+ , SO_4^{2-} , citric acid, and glucose the current change was less than $\pm 5\%$. Examination of histidine, glycine, and uric acid showed their tolerance limit about 10-fold compared to GP.

Analytical applications

The applicability of Ni-CA/MWCNT-CCE to the determination of GP was examined in the recovery of certain GP amounts in solution. Two concentrations of GP (33.82 and 49.88 $\mu\text{mol L}^{-1}$) were prepared and the corresponding LSVs were recorded at Ni-CA/MWCNT-CCE under optimum conditions. The recovery of GP was calculated by applying the peak currents in the calibration curve, obtaining the concentrations, and comparing them with the real amounts of GP. The recoveries for the two concentrations of GP used in this experiment were 100.06 and 98.97%, respectively.

Application of the proposed method was also tested by the analysis of GP tablets (100 mg tablet^{-1}). Figure 9a shows the LSVs of Ni-CA/MWCNT-CCE in a solution (50 $\mu\text{mol L}^{-1}$) prepared from GP tablets in a standard addition experiment. Figure 9b shows the standard addition

Table 1. Comparison of the efficiency of some modified electrodes in the electrochemical determination of GP

Electrode	$E_p / V \text{ vs. Ag/AgCl}$	Linear range / ($\mu\text{mol L}^{-1}$)	LOD / ($\mu\text{mol L}^{-1}$)	Sensitivity	Reference
Nickel oxide nanotube-modified carbon paste electrode	0.670	2.4-50	0.3	0.0163 $\mu\text{A } \mu\text{mol}^{-1} \text{ L}$	28
AgNP ^a /MWCNT-paste Electrode	-0.142	0.003-2.9 $\times 10^4$	0.00056	10.52 $\mu\text{A log}(\text{mol}^{-1} \text{ L})$	29
Gold electrode	0.68	0.3-15	0.13	0.2729 $\mu\text{A } \mu\text{mol}^{-1} \text{ L}$	27
Ni-CA/MWCNT-CCE	0.45	1.25-63.23	0.5	0.072 $\mu\text{A } \mu\text{mol}^{-1} \text{ L}$	Present work

^aAg nanoparticles.

plot. The average of 4 replicate measurements of GP was 97.3 ± 1.73 mg of GP per tablet. The accuracy and precision of the analysis were satisfactory in the determination of GP in formulations.

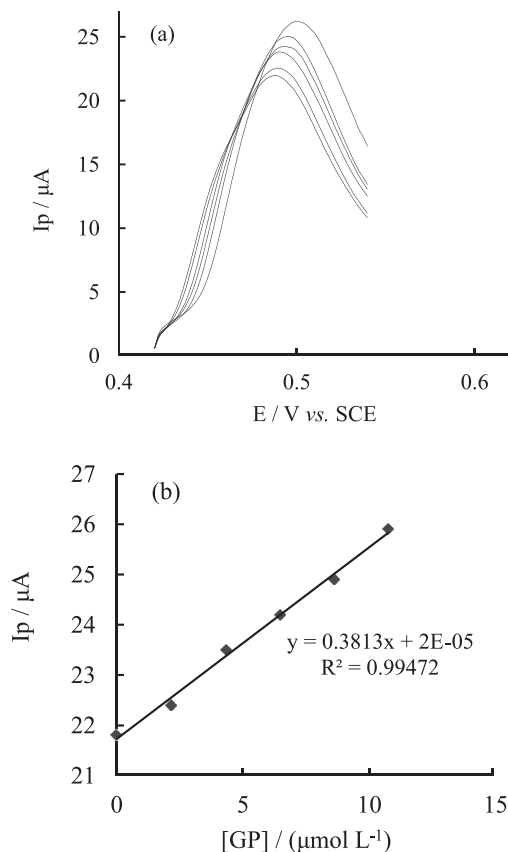


Figure 9. (a) LSVs for the determination of GP in tablets in NaOH (0.1 mol L^{-1}); (b) standard addition plot.

Conclusions

A carbon ceramic composite electrode was prepared in the presence of MWCNTs. Nickel-catechol complex was deposited electrochemically at the surface of the electrode. The porosity of ceramic materials, along with the improvement of electron transfer rate and large surface area provided by MWCNTs, made the electrode a proper microenvironment for the deposition of nickel complex. The prepared electrode showed good catalytic activity in the oxidation of gabapentin. The electrode had a long lifetime and shelf storage advantages, so can be used as the detector of gabapentin in flow system. The robustness of the electrode was advantageous in the polishing step, because of the resistance of CCEs to clogging and deformations, therefore, highly reproducible results were obtained. Determination of gabapentin in dosage forms by the proposed method was satisfactory with a recovery of $97.33 \pm 1.73\%$.

Acknowledgments

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