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Mediator-less highly sensitive voltammetric detection of glutamate using glutamate dehydrogenase/vertically aligned CNTs grown on silicon substrate

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ABSTRACT

A sensitive glutamate biosensor is prepared based on glutamate dehydrogenase/vertically aligned carbon nanotubes (GLDH, VACNTs). Vertically aligned carbon nanotubes were grown on a silicon substrate by direct current plasma enhanced chemical vapor deposition (DC-PECVD) method. The electrochemical behavior of the synthesized VACNTs was investigated by cyclic voltammetry and electrochemical impedance spectroscopic methods. Glutamate dehydrogenase covalently attached on tip of VACNTs. The electrochemical performance of the electrode for detection of glutamate was investigated by cyclic and differential pulse voltammetry. Differential pulse voltammetric determinations of glutamate are performed in mediator-less condition and also, in the presence of 1 and 5 μM thionine as electron mediator. The linear calibration curve of the concentration of glutamate versus peak current is investigated in a wide range of 0.1–500 μM. The mediator-less biosensor has a low detection limit of 57 nM and two linear ranges of 0.1–20 μM with a sensitivity of 0.976 mA mM^{-1} cm^{-2} and 20–300 μM with a sensitivity of 0.182 mA mM^{-1} cm^{-2}. In the presence of 1 μM thionine as an electron mediator, the prepared biosensor shows a low detection limit of 68 nM and two linear ranges of 0.1–20 with a calibration sensitivity of 1.17 mA mM^{-1} cm^{-2} and 20–500 μM with a sensitivity of 0.153 mA mM^{-1} cm^{-2}. The effects of the other biological compounds on the voltammetric behavior of the prepared biosensor and its response stability are investigated. The results are demonstrated that the GLDH/VACNTs electrode even without electron mediator is a suitable basic electrode for detection of glutamate.

1. Introduction

L-Glutamate plays an important role in food processing, biomedical, and clinical applications. It is an amino acid recognized as an important energy and nitrogen source in eukaryotic and mammalian cells. It functions as an excitatory neurotransmitter in the central nervous system and is believed to be responsible for certain fundamental processes such as learning, memory, neurodevelopment, biomaterial sensitivity, and synaptic plasticity. An increase in glutamate levels in the cerebrospinal fluids has been observed in neurological disorders, such as stroke, Alzheimer's, and Parkinson's diseases (Martin et al., 2000; Nedergaard et al., 2002). Therefore, accurate detection of glutamate concentration is critical in diagnostic and therapy of these kinds of diseases. The concentration of glutamate in extracellular space is in the range between 4 and 350 μM (Benveniste and Huttemeier, 1990; Hu et al., 1994) so the glutamate detection method must be linear in this range.

One of the most popular and simple methods for detection of glutamate is using of biosensor. Glutamate biosensors are usually based on the glutamate oxidase (GLOx) or glutamate dehydrogenase (GLDH). The GLOx catalyzes the oxidation of glutamate to 2-oxoglutarate in the presence of oxygen, producing H_2O_2, simultaneously. Quantification of glutamate is achieved via electrochemical oxidation of the liberated H_2O_2. However, the oxidation of H_2O_2 usually requires a relatively high positive over-potential. Many other electro active species such as ascorbic acid (AA) and uric acid (UA), which usually coexisting in the biological fluids, can also be oxidized at the high potential and their electrochemical signals thus severely affect the selectivity of the biosensor responses. The responses of the electrochemical biosensors based on GLDH involve

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the oxidation of enzymatically generated nicotinamide adenine dinucleotide (NADH, Eq. (1)) (Olson Cosford and Kuhr, 1996; Kuhr et al., 1993; Pantano and Kuhr, 1993).

$$\text{Glutamate} + NAD^+ + H_2O \xrightarrow{GLDH} \text{2-oxoglutarate} + NADH + NH_4^+ + H^+ \quad (1)$$

The selective detection of glutamate in the presence of other interfering compounds by the dehydrogenase-based biosensor can be successfully performed, when the electro-oxidation of NADH is achieved at less anodic potentials. The direct oxidation of NADH at unmodified electrodes requires large anodic over-potentials (>1 V), owing to the slow kinetics of the electron transfer (Moiroux and Elving, 1978). On the other hand, the responses of the unmodified electrodes usually suffer from fouling by the adsorption of the oxidation products. Various methodologies have been developed to facilitate the electron transfer kinetics for the oxidation of NADH (Gorton and Dominguez, 2002). One of them is the application of carbon nanotubes (CNTs) in various forms, especially as nanobiocomposite modified electrodes (Chakraborty and Retna Raj, 2007; Tang et al., 2007a,b; Rahman et al., 2009; Doaga et al., 2009; Meng et al., 2009). However, using directly grown CNTs is practically attractive since it can avoid the issue of CNT dispersion and transfer, offer a good attachment and an electrical connection with the substrates without using a binder and also provide a vertically aligned structure that avoids degradation of enzyme on the electrode surface. Furthermore, their attractive properties such as, high electrical and thermal conductivities, superior mechanical strength, wide electrochemical potential window, flexible surface chemistry (Li and Meyyappan, 2004; Li et al., 2005) and covalently attachment of enzyme on CNTs provide better electron transfer between active sites of the enzyme and electrode. For these reasons in the present work, vertically aligned carbon nanotubes (VACNTs) were used and GLDH enzyme covalently attached to the CNTs. Also, using VACNTs on silicon substrates for enzymatic assay, due to its compatibility with the standard Si micro-fabrication technology, can be considered as an effective methodology to integrate an array of sensors for lab-on-a-chip systems.

Previous researches have been shown the CNTs based electrodes alone are not sufficient enough for the selective detection of NADH (Musameh et al., 2002; Wang et al., 2003). However, in the present investigation, we described a mediator-less low potential detection of enzymatically produced NADH using only covalently attached GLDH on vertically aligned carbon nanotubes. The prepared biosensor is applied for the determination of glutamate in a wide range of concentration with nano-molar detection limits.

2. Experimental

2.1. Chemicals and reagents

Glutamic Dehydrogenase (GLDH, from bovine liver Type I, ammonium sulfate suspension, > 40 units/mg protein), L-Glutamic acid monosodium salt hydrate (>99%, TLC), N-hydroxysulfosuccinimide sodium salt (sulfo-NHS) were purchased from Sigma/Aldrich. All other chemicals used in this investigation were of analytical reagent grade and purchased from Merck. All solutions were prepared in deionized water (18.2 MΩ, Millipore Milli-Q system). 0.1 M of phosphate buffer solution was employed as supporting electrolyte. Solutions of GLDH and NAD^+ were freshly prepared using phosphate buffer solution of pH 7.0, immediately before each experiment. All voltammetric investigations were performed in deoxygenated solutions by purging the highly pure nitrogen.

2.2. Apparatus

Electrochemical experiments were performed with an IVIUM COMPACSTAT potentiostat/galvanostat in a three electrode setup using an o-ring Teflon cell consisting of VACNTs as working electrode, an Ag/AgCl reference electrode, and a platinum counter electrode. A nitrogen atmosphere was kept over the solution during measurements. The SEM experiments were performed on a Hitachi SE4160 field emission SEM.

2.3. Synthesis of VACNTs

Prior growth of VACNTs, the p-type (100) silicon wafer was highly doped with phosphorous using a diffusion furnace at a temperature of 800 °C and with $POCl_3$ liquid source to create the contact layer for electrochemical analysis. Typical value of the wafer resistance was obtained about $5.4 \times 10^{-3}\ \Omega$ cm. A Ni catalyst film of 8–10 nm thickness was deposited on the highly doped silicon wafer using electron beam evaporation. VACNTs were grown on the Ni film using DC-PECVD method. Before the growth process, a hydrogenation step for 5 min was carried out to form Ni nano-islands at a temperature of 650 °C. The CNT growth carried out in a mixture of C_2H_2/H_2 (5/18 sccm) at a pressure of 1–5 Torr, temperature of 650 °C and power of 4 W/cm^2.

2.4. Immobilization of the enzyme on VACNTs

Fig. 1 shows schematic of different steps for immobilization of the enzyme. The CNTs were pretreated in Ni etchant (H_2SO_4:HNO_3:H_2O (10:10:50)) for 20 min and in 10% HF solution to expose contact layer and then were dried on vacuum condition to prevention cohesive tip of nanotubes together. For convert various oxides at the CNT tips into mostly carboxylic acid groups (–COOH), which are necessary for covalent binding of the enzyme to the VACNTs, electrochemical treatment was done in 1 M NaOH at 1.5 V for 30 s (Arumugam et al., 2009). In the next step, GLDH was attached onto the end of the CNTs using 1-(3-dimethylamino propyl)-3-ethylcarbodiimide hydrochloride (EDC) and hydroxy-sulfosuccinimide sodium salt (sulfo-NHS) to promote amide linkages between the carboxyl-terminated nanotubes and the lysine residue of the protein. This was done by immersing the electrode in 1 mL of freshly prepared phosphate buffer solution (PBS) containing 10 mg/mL EDC and 30 mg/mL sulfo-NHS solution that was mixed carefully using a syringe needle. The reaction was allowed to occur at room temperature for 2 h. Then, after removing the excess solution of EDC and sulfo-NHS, 0.5 mL of enzyme (4 mg/mL in PBS) was placed on the electrode surface and the reaction was allowed to complete between the functionalized CNTs and the enzyme at room temperature for 2 h in the stirred solutions. Finally, the electrode was washed with a 0.1 M PBS of pH 7.4 containing 0.2% bovine serum albumin (BSA) and stored at 4 °C before use.

3. Results and discussions

3.1. Morphological characterization of VACNTs

Fig. 2A depicts SEM images of the grown VACNTs. The average diameter of the CNTs was varied from 70 to 100 nm and the average length was controlled at about 1 μm. Nanotube's walls dimension are comparable with enzyme dimension, so they are suitable for covalently attachment of the enzyme on tip of the CNTs. Fig. 2B depicts SEM images of VACNTs after removing of Ni catalysts from the tip of CNTs. It shows that Ni nanoparticles are successfully removed from the tips by a simple method without any aggregation

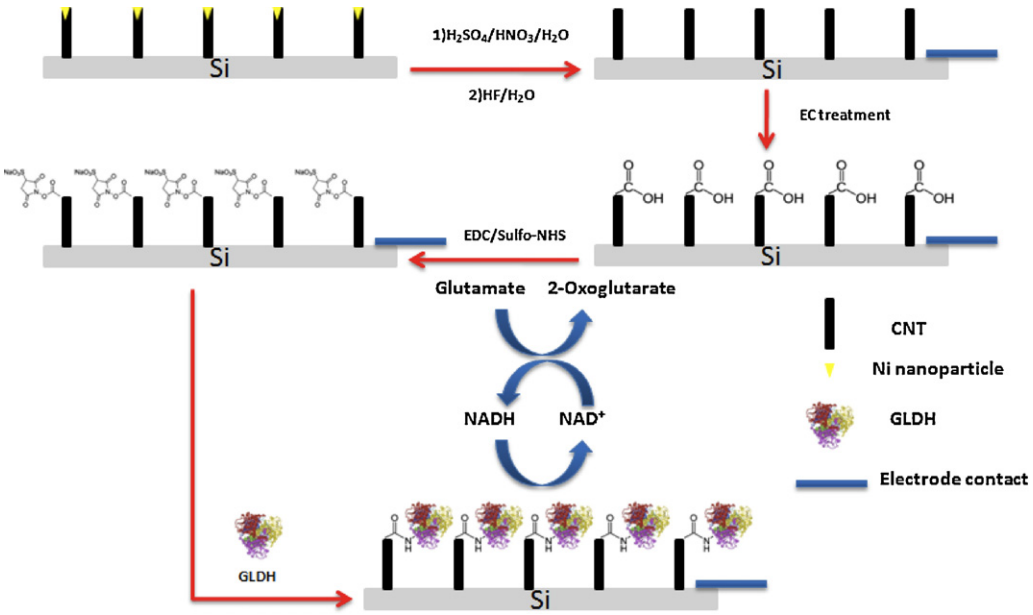

Fig. 1. Schematic plan of immobilization steps of electrode surface.

of them. Fig. 2C shows VACNTs after the biosensor has been used continually for two weeks. As can be seen, they still remain vertical after 4 h stirring and several measurements of the analyte. These results showed that the structural stability of the biosensor is suitable for analytical purposes.

3.2. Electrochemical characterization of VACNTs electrode

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were applied for the evaluation of the electrochemical properties of unmodified VACNTs. Fig. 3A shows cyclic voltammograms of VACNTs at the potential scan rates of 5–80 mV s^{-1}, obtained in solution containing 5 mM $K_3[Fe(CN)_6]$ and 1 M KCl. A quasi reversible electrochemical process can be proposed, according to the increase of the peak potential separation (ΔE_p) with the scan rate. Furthermore, it shows that the observed anodic and cathodic peak currents were directly proportional to square root of the scan rate ($\upsilon^{1/2}$). Such a behavior implies that the redox process is controlled by linear diffusion of the electroactive species, which is expected for high density VACNTs. Fig. 3B shows EIS spectra of VACNTs at different amplitudes with 0 V dc signal (vs. Ag/AgCl) in 0.1 M phosphate buffer of pH 7.4 containing 5 mM $K_3[Fe(CN)_6]$, 5 mM $K_4[Fe(CN)_6]$ and 0.1 M KCl. Electrochemical impedance spectra have a meaningful interpretation only if

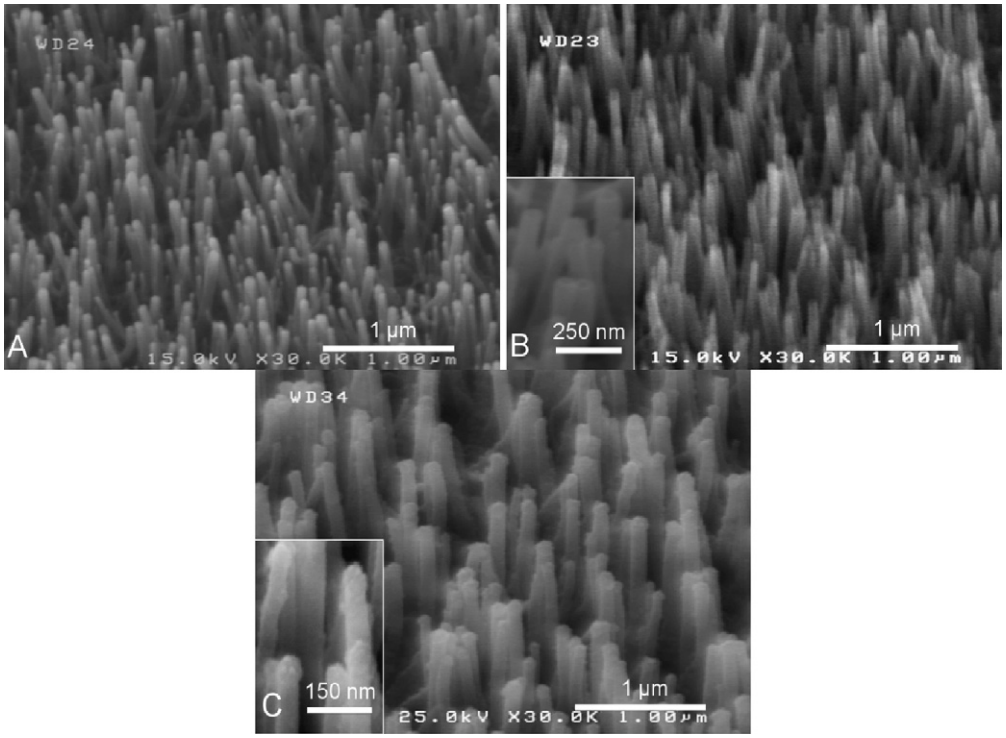

Fig. 2. FESEM images of VACNTs before (A), after remove of Ni (B) and after immobilization of enzyme (C).

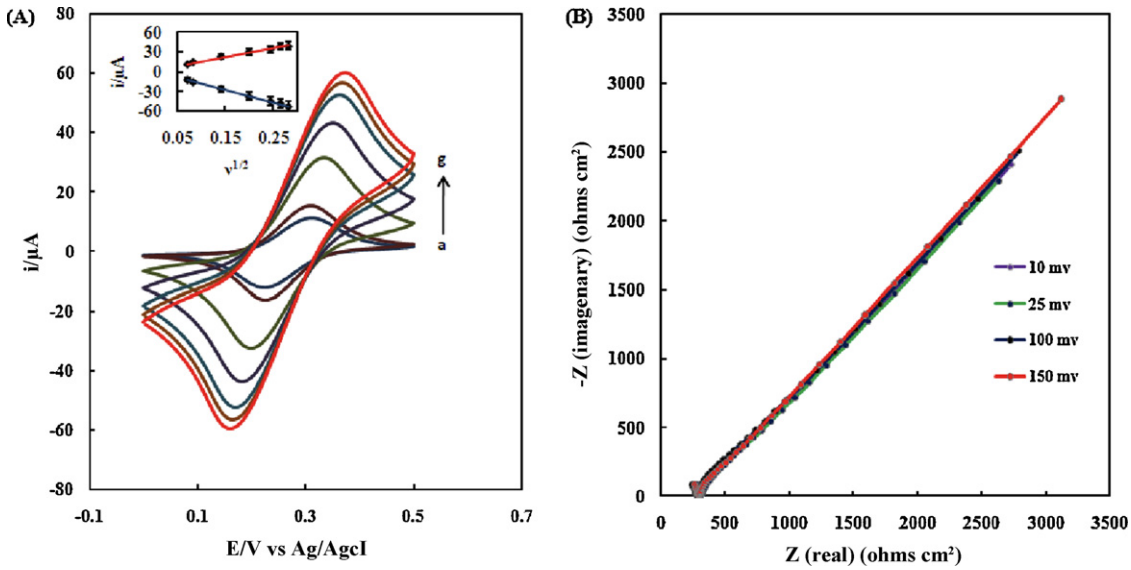

Fig. 3. Cyclic voltammograms of unmodified electrode in 5 mM $K_4[Fe(CN)_6]$ and 1 M KCl at scan rate of (from curves a to g) 5,7,20, 40, 60 and 80 mV s^{-1}. Inset: plots of I_p vs. $\upsilon^{1/2}$. (A) Linearity of unmodified VACNTs, Impedance curves were taken at different amplitudes. A solution of 5 mM $K_4Fe(CN)_6$/5 mM $K_3Fe(CN)_6$, 0.1 M KCl in 0.1 M phosphate buffer (pH 7.4) (1:1 mixture) was used. The spectra were taken at 0.1 Hz to 100 kHz and 0 V dc potential vs. Ag/AgCl (B).

the electrochemical cell behaves linearly. In this condition, the cell impedance is independent from amplitude plot; ideally one should not observe any changes as the amplitude of the applied voltage is varied. However, in nonlinear electrochemical cells an ideal behavior cannot be observed. In order to maintain linearity of the cell during the measurement process, an ac signal of very small amplitude is generally applied. However, such small amplitudes give rise to poor S/N ratio and are not suitable for sensitive measurements. One way to reduce the noise is to increase the amplitude of the applied voltage. But, this causes to introduce the nonlinearity into the system, which makes it difficult to interpret the spectrum using simple circuit models. In most studies, it was shown that impedance data are meaningful only when ac signal of amplitude <25 mV is applied (Barbero et al., 2005). According to the EIS spectrum, linearity is observed even at high amplitudes, so this electrode can be considered as a good candidate for high amplitude EIS studies.

3.3. Electrochemical behavior of glutamate at the GLDH/VACNTs electrode

The activity of the enzymatic biosensors shows high dependency to pH, temperature and the concentration of the coenzyme. These conditions were optimized in this work. The highest electrocatalytic activity of the prepared biosensor was obtained in a temperature of 42 °C, pH of 7.0 and a concentration of 2 mM of NAD^+. The results showed that in higher concentrations of NAD^+ the response of the biosensor reaches to a relatively stable value and stays practically constant afterward (insets (I, II) of Fig. 4A).

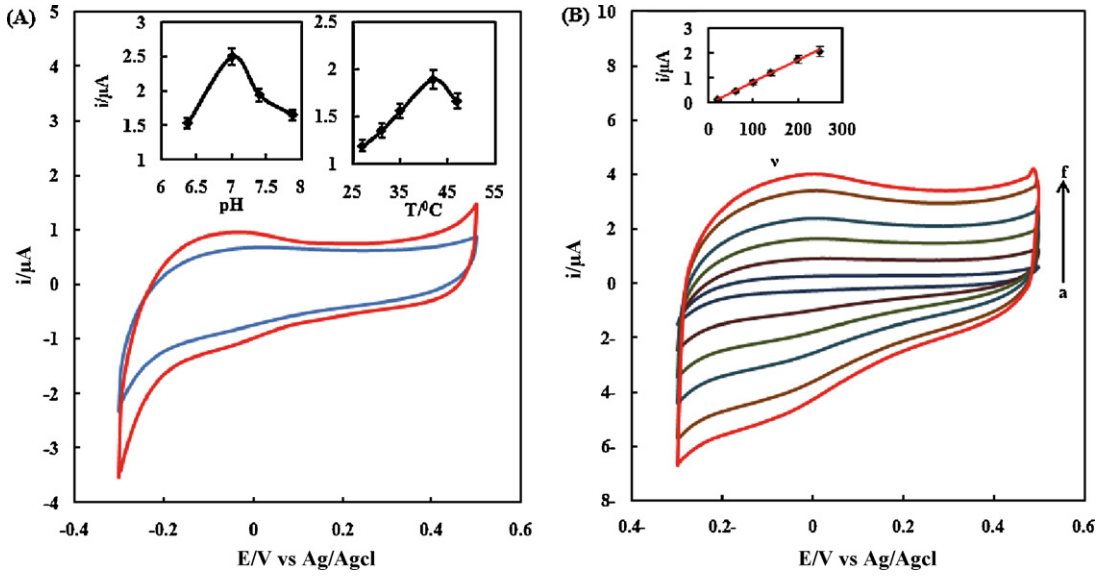

Fig. 4. Voltammetric responses of the electrode in phosphate buffer solution (0.1 M, pH 7) containing 2 mM NAD^+ in the absence (blue curve) and presence (red curve) of 0.3 mM glutamate. (A) The inset (I) and (II) show the dependence of the electrocatalytic current of the electrode on the solution pH (I) and the performing temperature (II), respectively. Cyclic voltammograms of the electrode in phosphate buffer solution (0.1 M, pH 7) containing 2 mM NAD^+, and 0.3 mM glutamate at scan rate of (from curves a to f) 20, 60, 100, 140, 200, 250 mV s^{-1} (B). (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

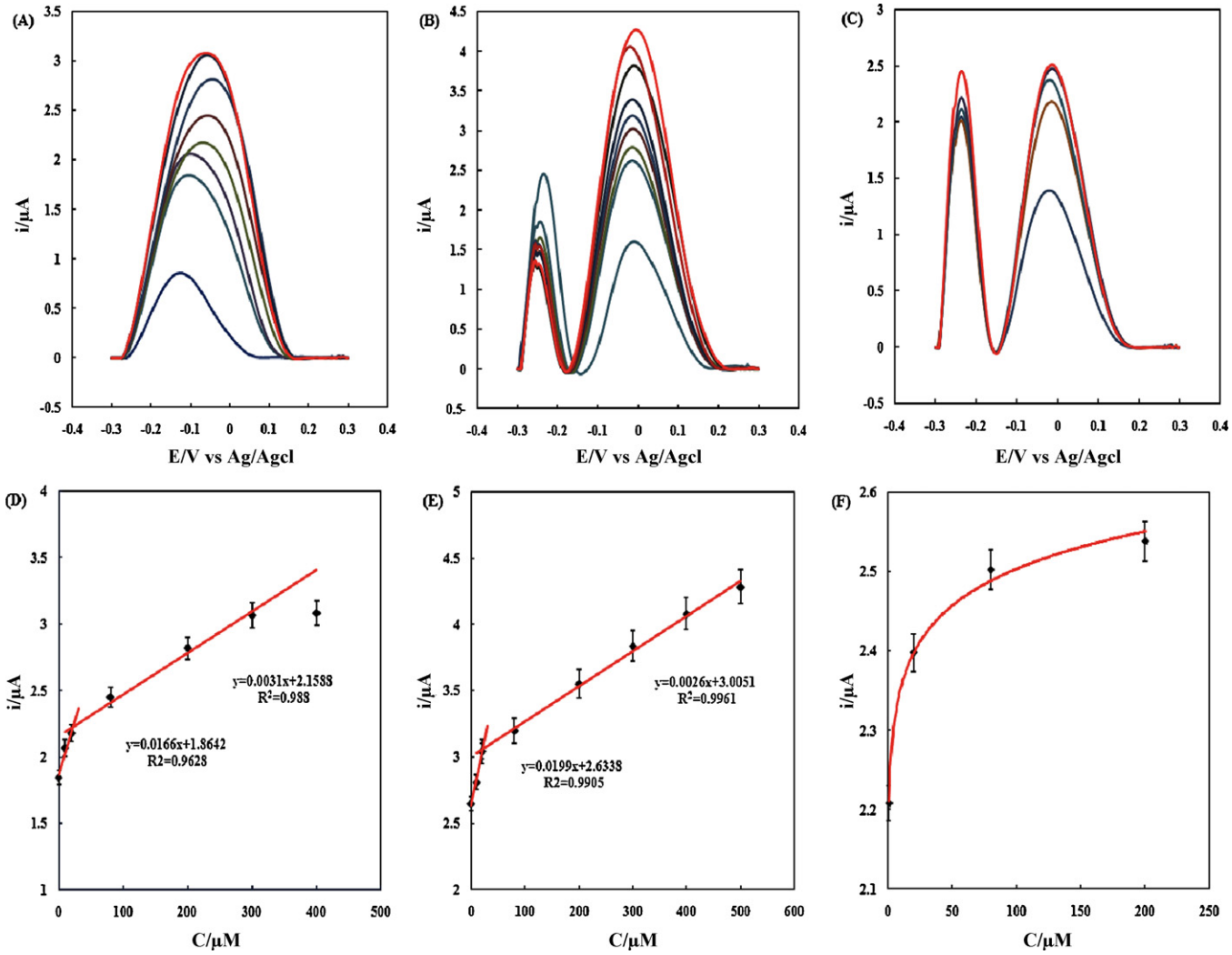

Fig. 5. DPVs recorded in phosphate buffer solution (0.1 M, pH 7) containing: 2 mM NAD^+, 0 μM thionine at 0, 0.1, 10, 20, 80, 200, 300 and 400 μM glutamate (A), 1 μM thionine at 0, 0.1, 10, 20, 80, 200, 300, 400 and 500 μM glutamate (B), 5 μM thionine at 0,10,20,100,200 μM glutamate (C). Calibration curve of different glutamate concentrations on: mediator-less electrode (D), electrode based on 1 μM thionine (E), electrode based on 5 μM thionine (F). In each case, pulse amplitude was 50 mV.

Therefore, these values were selected as the optimum experimental conditions in all electrochemical analysis.

Cyclic voltammograms (CVs) of the immobilized VACNTs obtained in PBS of pH 7.0 containing 2 mM NAD^+ and also, same buffer solution containing 0.3 mM glutamate at the scan rate of 50 mV s^{-1} (Fig. 4A). Upon addition of 0.3 mM glutamate, an anodic peak, resulted from the electrocatalytic oxidation of NADH, is appeared at −0.084 V. In comparison to most reported glutamate biosensors based on GLDH, the anodic peak potential for the NADH oxidation is observed in lower potential (Chakraborty and Retna Raj, 2007; Tang et al., 2007a,b; Rahman et al., 2009; Doaga et al., 2009). The low detection potential can significantly reduce the influence of easily oxidizable species. Increasing of the glutamate concentration leads to the enhancement of the anodic peak current. The corresponding peak current is increases linearly with the potential scan rate (in the range of 20–250 mV s^{-1}) (Fig. 4B). Such a behavior indicating that the overall electrochemical process is a surface absorbed reaction.

3.4. Analytical applications

The analytical performance of the glutamate biosensor was explored by using differential pulse voltammetry (DPV) method. Another aim of this work was to examine the performance of biosensor without application of any electron mediator and also, in the presence of the different concentrations of thionine. DPV measurements were conducted from −0.3 to +0.3 V vs. Ag/AgCl in 0.1 M PBS solution of pH 7.0. Fig. 5A, B, C displays DPVs for the various concentrations of glutamate (0.1–500 μM) in the absence of the mediator and in the presence of 1 μm and 5 μm thionine, respectively. The peak current at −0.068 V showed to be dependent on glutamate concentration at mediator-less condition. Addition of 1 μm thionine as an electron mediator caused the peak corresponding to glutamate getting to be sharp and also shifted to −0.012 V. The peaks at −0.2 V is assigned to thionine and Fig. 5 D, E, F show the corresponding calibration curves. In order to calculate the sensitivity, the effective surface area of the electrode could be obtained according to the Randles–Sevcik equation. CV experiments of 5 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl are performed in various potential sweep rates for the enzyme-immobilized VACNTs electrode. A slope of the straight line of $I_{p,a}$ vs. $\upsilon^{1/2}$ is resulted as 62.45 μA $s^{1/2}$ $V^{-1/2}$ ($R^2 = 0.999$). Regarding $n = 1$ and $D = 7.6 \times 10^{-6}$ cm s^{-2} for $K_3[Fe(CN)_6]$, the effective surface area of the electrode is estimated to be 0.0173 cm^2.

The mediator-less electrode exhibited a sensitivity of 0.976 mA mM^{-1} cm^{-2} in the range of 0.1–20 μM glutamate, and 0.182 mA mM^{-1} cm^{-2} in the range of 20–300 μM with a low detection limit of 57 nM. The electrode based on 1 μM thionine

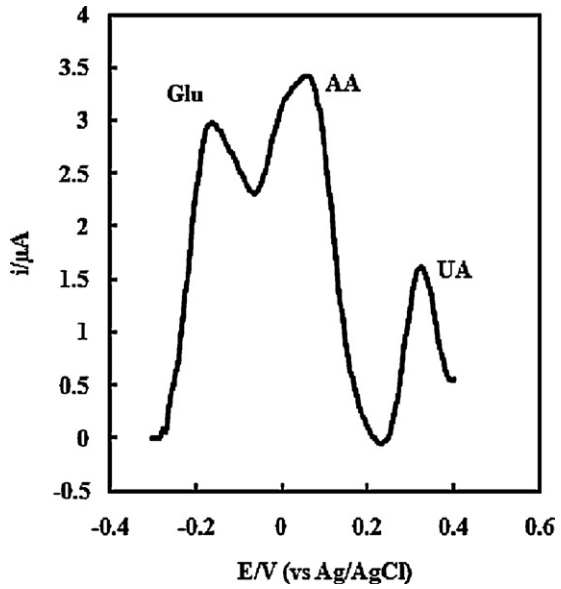

Fig. 6. DPV illustrating the interference free sensing of glutamate at electrode in 0.1 M PBS of pH 7, 2 mM NAD^+ and glutamate, AA, and UA (0.2 mM each), also demonstrating simultaneous sensing of glutamate, AA and UA. Pulse amplitude was 50 mV.

showed a sensitivity of 1.17 mA mM^{-1} cm^{-2} in the range of 0.1–20 μM glutamate and 0.153 mA mM^{-1} cm^{-2} in the range of 20–300 μM with a low detection limit of 68 nM. Inactivation of some enzyme sites with thionine may be cause of little reduction of the sensitivity in the presence of thionine in high concentration range of glutamate. However, increasing of thionine concentration to 5 μm caused to a considerable decrease in the performance of biosensor, which may be due to irreversible surface covering of the electrode in higher concentrations of thionine, so this biosensor can be used without using any mediator and also, in the presence of 1 μm thionine. The obtained linear range is useful, since the normal glutamate concentration in extracellular space is in the range between 4 and 300 μM (Hu et al., 1994), suggesting that the GLDH/VACNTs electrode can be used as a biosensor glutamate sensing in the physiological levels. The limit of detection is estimated to be ca. 57 and 68 nM (at S/N = 3) for mediator-less and in the presence of 1 μM thionine, respectively. The obtained results are much better than that obtained using the glutamate microbiosensor based on GlOx (2.5 μM) (Schuvailo et al., 2006) and also by the thionine/single-walled carbon nanotubes composite modified electrode (0.1 μM; Meng et al., 2009). The linear response range is wider than those previous reports by Tang: 0.2–250 μM (Tang et al., 2007a) and also reported by Meng: 0.5–400 μM (Meng et al., 2009). The sensitivity is also higher than that acquired previously by Meng in the range of 20–300 μM (137.3 μA mM^{-1} cm^{-2}) (Meng et al., 2009) and much higher than that obtained using thionine/MWCNTs Composite Film on Gold Substrates in the range of 0.1–500 μM (281.6 μAmM^{-1} cm^{-2}) (Rahman et al., 2009).

Selective determination of glutamate is one of the main challenges in the development of glutamate sensor. The electrooxidation of AA and UA interferes in the voltammetric determination of NADH at the unmodified electrode. In the present investigation, the analytical performance of the CNT composite electrode towards NADH in the presence of the common interferential species such as, AA and UA has been investigated. For this reason, DPV experiments were performed in 0.1 M PBS of pH 7.0 containing 2 mM NAD^+ and 0.2 mM of each of glutamate, AA and UA. As can be seen in Fig. 6, the electrode does not suffer from the interferences of AA and UA. The results show individual voltammetric peaks at −0.168, 0.068 and 0.324 V for glutamate, AA, UA, respectively. Since the separation between the voltammetric peaks is large enough, the selective and simultaneous sensing of these compounds is feasible with this modified electrode.

The stability of the biosensors is a critical feature for their successful applications. Just as SEM image shows in Fig. 2C, the structure stability of the vertically aligned morphology of the CNTs is suitable for biosensor applications. Furthermore the storage stability of the GLDH/VACNTs biosensor was studied when it was stored in phosphate buffer at 4 °C for two weeks. The response of the biosensor toward 0.1 mM glutamate was recorded at 2 days intervals. The DPV experiments responses after three days reaches from 2.354 μA to 2.22 μA and still retains 94.3% of its original response. Even after the biosensor has been used for two weeks (three measurements each two days) its response still remains at 80.5% of the initial value (1.88 μA). The results showed that the GLDH/VACNTs electrode is compatible with the immobilized enzyme and is helpful to maintain the bioactivity of GLDH on electrode surface.

4. Conclusions

Results presented herein demonstrate GLDH/VACNTs on highly doped silicon electrode without any enzyme stabilizer polymers or metallic contact layer can be used as glutamate biosensor at low over potential. Also, even without any environmental hazardous phenothiazine compounds such as thionine as electron mediator, this electrode shows excellent analytical performances such as, low detection limit (57 nM), high sensitivities at two concentration ranges of glutamate between 0.1–20 μM (0.976 mA mM^{-1} cm^{-2}) and 20–300 μM (0.182 mA mM^{-1} cm^{-2}) and good selectivity and stability. Therefore, this biosensor would have a good potential for the glutamate determination in health care fields and also in vivo experiments.

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