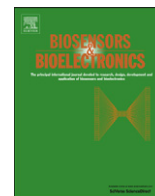




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Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

Electrocatalytic oxidation and determination of insulin at nickel oxide nanoparticles-multiwalled carbon nanotube modified screen printed electrode



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ARTICLE INFO

Article history:

Received 13 November 2012

Received in revised form

16 January 2013

Accepted 21 January 2013

Available online 13 February 2013

Keywords:

Insulin

Nickel oxide nanoparticles

Amperometric detection

Electrodeposition

Screen printed electrode

ABSTRACT

Nickel oxide nanoparticles modified nafion-multiwalled carbon nanotubes screen printed electrode (NiONPs/Nafion-MWCNTs/SPE) were prepared using pulsed electrodeposition of NiONPs on the MWCNTs/SPE surface. The size, distribution and structure of the NiONPs/Nafion-MWCNTs were characterized by transmission electron microscopy (TEM) and x-ray diffraction (XRD) and also the results show that NiO nanoparticles were homogeneously electrodeposited on the surfaces of MWCNTs. Also, the electrochemical behavior of NiONPs/Nafion-MWCNTs composites in aqueous alkaline solutions of insulin was studied by cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy (EIS). It was found that the prepared nanoparticles have excellent electrocatalytic activity towards insulin oxidation due to special properties of NiO nanoparticles. Cyclic voltammetric studies showed that the NiONPs/Nafion-MWCNTs film modified SPE, lowers the overpotentials and improves electrochemical behavior of insulin oxidation, as compared to the bare SPE. Amperometry was also used to evaluate the analytical performance of modified electrode in the quantitation of insulin. Excellent analytical features, including high sensitivity ($1.83 \mu\text{A}/\mu\text{M}$), low detection limit (6.1 nM) and satisfactory dynamic range (20.0–260.0 nM), were achieved under optimized conditions. Moreover, these sensors show good repeatability and a high stability after a while or successive potential cycling.

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1. Introduction

Insulin is a polypeptide hormone that contains one intra chain and two inter chain disulfide bonds (supplementary material, S1). It serves as a predictor of diabetes of insulinoma and trauma (Melloul et al., 2002; Tannuri et al., 1993) and it is used to control glucose levels in blood within a narrow concentration range (Wang et al., 2007). The direct monitoring of insulin in a diabetic patient has a better prospect in clinical investigation rather to the glucose measurement (Snider et al., 2008; Kivlehan et al., 2008). Therefore, a fast and simple method for accurate detection of insulin is very important.

Several methods have been explored for the quantitative analysis of insulin including enzyme-linked immunosorbent assay (Kumada et al., 2007), radioimmunoassay (Murayama et al., 2006), high performance liquid chromatography (HPLC) (Mercolini et al., 2008) and capillary electrophoresis (Ortner et al., 2009). However, these methods are time-consuming, cumbersome, and very costly. Direct electrochemical detection of insulin is simple and inexpensive and also is attractive as it can provide sensitivity and reduces analysis

time to enable continuous real-time measurements compared to the above methodologies (Snider et al., 2008). However, direct oxidation of insulin at conventional electrodes is limited by the slow kinetics and surface fouling onto electrochemical devices (Zhang et al., 2005). Furthermore, low sensitivity, reproducibility and stability over a wide range of solution compositions and high overpotential at electrodes are other limitations of unmodified electrodes as an electrochemical sensor for insulin detection (Salimi et al., 2008). Therefore, several electrochemical sensors (Wang et al., 2007; Zhang et al., 2005; Salimi et al., 2007; Salimi et al., 2008; Cox and Gray, 1989; Gorski et al., 1997; Pikulski and Gorski, 2000; Cheng et al., 2001; Arvinte et al., 2010) were fabricated for trace and even ultra-trace level detection of insulin.

Transition metals occur in biological systems because they have multiple oxidation states separated by only modest potentials, which make them suitable candidates for electron-transfer processes. Nickel is of particular interest as modifying agents because in basic media nickel redox centers show high catalytic activity towards the oxidation of some organic compounds (Casella et al., 1993; Ciszewski, 1995) at a relatively low cost, compared to other (especially, noble metal) catalysts.

Carbon nanotubes (CNTs) have attracted much attention due to their unique properties. As electrode modifiers, CNTs show negligible surface fouling (Pumera, 2009), decreased overpotential,

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increased voltammetric currents, they can be used for promoting electron transfer between the electroactive species and the electrode (Wang, 2005) and provide a new method for fabricating electrochemical sensors or biosensors. It is well known that high-surface-area CNT when combined with metal nanoparticles or metal oxides can improve the performance of the final material (Arvinte et al., 2011). The antifouling properties of nickel oxide nanoparticles for insulin, thiols, disulfides and their oxidation products have been reported either (Salimi et al., 2008). Recently, the preparation of a CNT-nickel-cobalt oxide modified graphite screen printed electrode and its use in the electrocatalytic oxidation of insulin was reported by Arvinte et al. (2010). The modification was achieved by adsorption of NiCoO₂ at a graphite screen printed electrode.

In this work, we have reported a NiONPs/Nafion-MWCNTs modified screen printed electrode which is prepared by the electrochemical pulsed potential deposition of the modifier. In fact, special properties of nano NiO are used rather than NiO crystals as active sites on the MWCNTs.

The electrochemical behavior of NiONPs/Nafion-MWCNTs composites in aqueous alkaline solutions of insulin was studied by cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy. Amperometry was also used for quantitative measurement of insulin.

2. Experimental

2.1. Chemicals and materials

Multiwalled carbon nanotubes with purity 95% (20–40 nm diameter and 1–10 μm length) were obtained from Research Institute of Petroleum Industry (Tehran, Iran). Nafion 5% solution and bovine insulin (≥ 27 USP units/mg) were purchased from Sigma. All other solvents and reagents were purchased from Aldrich or Merck and were used without further purification. A stock solution of insulin (0.20 mM) was prepared daily by dissolving powdered insulin in water and adding 10.0 μl of 1.0 M HCl to dissolve the powder. Insulin solutions were prepared by diluting aliquots of the insulin stock solutions with a carrier solution. All solutions were prepared with doubly distilled water. Insulin solutions were freshly prepared just prior to use and all experiments were carried out at room temperature.

2.2. Instruments

All electrochemical experiments were performed by using Autolab potentiostat/galvanostat type 30 (2) (Eco Chemie, Netherlands), equipped with FRA and GPES 4.9 software. A screen-printed carbon electrode (SPE) (3 mm in diameter) from Dropsens (Spain) was used as a planar three electrode based on a graphite working electrode, a carbon counter electrode and a silver pseudo-reference electrode. The electrode was rinsed in deionized water and preconditioned in 0.10 M HCl solution by potential scanning in –0.4 to +1.0 V at a scan rate of 100 mV s^{–1}. For the amperometric measurements, the modified SPE was immersed in the stirred NaOH solution, applying constant potential. EIS experiments carried out with a dc-offset potential of 550 mV and in the frequency range of 100,000 to 0.01 Hz. Transmission electron microscopy (TEM) image was determined with a Philips CM10 TEM. A personal computer was used for data storage and processing.

2.3. Preparation of modified electrode

MWCNTs were carboxylated (Ryu et al., 2009). The MWCNTs were washed with doubly distilled water and dried in vacuum at 80 °C. MWCNTs (10 mg) and 5.0 μl of 5.0% nafion solution were

dispersed in 5.0 ml water with ultrasonication for 1 h to get a homogenous suspension. 10.0 μl of the suspension was casted onto the surface of screen printed electrode and dried at room temperature.

The deposition bathes, were prepared using Ni(NO₃)₂ · 6H₂O with a concentration of 40.0 mM. The pH of the bath was adjusted in 2.0 using boric acid and some drops of sulfuric acid. The pulse potential for making NiONPs on the electrode was applied using –0.4 V for 0.3 s and 0.0 V for 2.5 s (supplementary material, S2). The sizes of particles were controlled by changing the number of applied pulses in the depositions. Clearly the increasing of the pulses caused to the formation of a larger particle of modifier at the surface of Nafion-MWCNTs/SPE. The prepared electrode was conditioned in 0.10 M NaOH solution by potential cycling between 100 to 700 mV for about 10 cycles of potential scans with a sweep rate of 100 mV s^{–1}. These guidelines were obtained experimentally as best values for complete transformation of Ni (II) to Ni (III) and maximum activation of electrode surface towards electrocatalytic oxidation of insulin. All electrochemical investigations were performed at room temperature.

3. Results and discussion

3.1. Morphological characterization of the NiONPs/Nafion-MWCNTs/SPE

The surface morphology and elemental composition of the NiONPs/Nafion-MWCNTs/SPE was characterized by TEM image and XRD, respectively (as shown in Fig. 1). The structure of the composite showed a homogeneous film on the surface of SPE. Particles with diameter below 30.0 nm are observed in the TEM image, indicating a nanostructure for the NiO deposited film on the Nafion-MWCNTs/SPE (Fig. 1A). It is known that carboxylic acid groups on the surface of MWCNTs can stimulate the deposition of NiO nanoparticles (Jin et al., 2007; Golovin et al., 2011).

It is known that the physico-chemical properties of the NiO nanoparticles are very different from bulk NiO crystals (Rao and Cheetham, 2006). An example of this is the high surface area and excellent magnetic properties of ferromagnetic NiO nanocrystals which has attracted considerable attention than the bulk NiO. Thus, using the electrochemical pulsed deposition method, it is possible to obtain a structure including NiO nanoparticles with a narrow size distribution arranged in the framework of CNTs. Furthermore, electrochemical pulsed deposition prevents agglomeration of nanoparticles and makes it possible to control the film thickness by varying the experimental parameters. Such an electrode exhibits an excellent stability, a high surface coverage and an electrocatalytic activity toward the oxidation of insulin by various electrochemical methods.

In order to further support the formation of NiONPs-MWCNTs composite, the X-ray diffraction (XRD) profile of the prepared nanocomposite was also obtained and the result is shown in Fig. 1B (XRD data, supplementary material).

3.2. Study of electrochemical behavior of NiONPs/Nafion-MWCNTs

Electrochemical behavior of NiONPs/Nafion-MWCNTs was studied in 0.10 M NaOH solution. In these voltammograms (supplementary material, S3), a pair of well-defined peaks is observed for Ni oxide as was reported previously. These peaks are due to conversion of Ni(II)/Ni(III) to each other in the alkaline solution via the following reaction (Asgari et al., 2011; Golikand et al., 2006):



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