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Electrochemical behaviour of carbon paste electrodes enriched with tin oxide nanoparticles using voltammetry and electrochemical impedance spectroscopy

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ABSTRACT

The effect of the SnO_2 nanoparticles (SNPs) on the behaviour of voltammetric carbon paste electrodes were studied for possible use of this material in biosensor development. The electrochemical behaviour of SNP modified carbon paste electrodes (CPE) was first investigated by using cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) techniques. The performance of the SNP modified electrodes were compared to those of unmodified ones and the parameters affecting the response of the modified electrode were optimized. The SNP modified electrodes were then tested for the electrochemical sensing of DNA purine base adenine to explore their further development in biosensor applications.

1. Introduction

Tin dioxide (SnO_2) is a material with versatile applicability in a large number of physicochemical procedures. Thin films composed by SnO_2 nanoparticles can be applied as the nanofiltration membranes [1], anticorrosion coatings [2] and photocatalysts in the degradation of organic molecules in aqueous medium [3]. Further, SnO_2 nanoparticles have been reported as a very promising material for new-generation, high-performance gas-sensing devices by reason of the relatively low operating temperature and also they can be used to detect both reducing gases and oxidizing ones by adding various doping agents [4–7].

These aspects play a key role also in the use of tin oxide for electrochemical applications, i.e., as an anode in Li-ion batteries [8,9], or as an active matrix hosting precious metals for electrocatalytic processes [10,11]. Due to the conductive properties of tin oxide, the SnO_2 nanoparticles have been used for the modification of electrochemical transducers in sensor applications [12–14]. In all these applications a prerequisite is the preparation of nanocrystalline tin oxide with a small particle size [15].

Various type of affinity sensors have been rapidly developed combined with different nanomaterials towards the goal of simple and low-cost point-of-care detection of specific nucleic acid sequences, proteins, toxins etc. [16]. The nanoscale sensors based on nanoparticles, nanowires, nanotubes and other nanomaterials have recently received considerable attention [16–23].

In the study of Ansari et al. [12], a chitosan-tin oxide nanobiocomposite film was deposited onto the surface of indium-tin oxide glass plate for the preparation of platform to detect cholesterol using cyclic voltammetry. Direct electrochemistry and electrocatalysis of horseradish peroxidase immobilized on sol-gel derived SnO_2/gelatin composite film was studied by Jai et al. [13]. The nanocrystalline SnO_2 electrodes were developed for the detection of two protein: cytochrome *c* and hemoglobin, by using cyclic voltammetry and spectroelectrochemistry without the use of any electron-transfer promoters or mediators [14].

SnO_2 nanoparticles of 3–4 nm size synthesized by hydrothermal method [24] were used in this study for development of an electrochemical biosensor. Firstly, the electrochemical behaviour of SNP modified carbon paste electrodes (SNP-CPE) was examined with regard to unmodified ones (CPE) by using cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS). The overall performance of SNP modified sensor were then investigated, and discussed in terms of optimum analytical conditions, such as; the effect of scan rate, the pretreatment procedure, and also the nanoparticle fraction in graphite matrix upon the sensor response. The electrochemical monitoring of DNA purine base, adenine was then performed by using unmodified CPE and SnO_2 nanoparticles modified CPE.

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2. Experimental

2.1. Materials and method

All electrochemical measurements using the differential pulse voltammetry (DPV), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried by using AUTOLAB – PGSTAT 302 electrochemical analysis system supplied with a FRA 2.0 module for impedance measurements, and GPES 4.9 software package (Eco Chemie, The Netherlands). The three electrode system was consisted of the carbon paste electrode (CPE), an Ag/AgCl/KCl reference electrode (BAS, Model RE-5B, W. Lafayette, USA) and a platinum wire as the auxiliary electrode. All measurements were performed in the faraday cage (Eco Chemie, The Netherlands).

All chemicals were in analytical grade and used without further purification. Graphite powder and mineral oil were purchased, respectively, from Fluka and Sigma. Adenine was purchased from Sigma. Other chemicals were in analytical reagent grade and they were supplied from Sigma or Merck. Ultrapure water was used in all solutions. 1000 μg/mL adenine stock solution was prepared in 0.5 M acetate buffer solution containing 20 mM NaCl (ABS, pH 4.80) and all dilutions were performed using ABS.

SnO_2 nanoparticles of 3–4 nm size synthesized by hydrothermal method [24] were used in this study. These particles were earlier characterized by X-ray diffraction and transmission electron microscope analysis [24].

2.2. Electrode preparation

The SNP modified carbon paste (SNP-CP) was prepared in two steps: The first step involved a through mixing of the desired amounts of graphite powder of 20 μm particle size and mineral oil (30/70%, w/w graphite/oil). Then, a desired amount of SNP was hand mixed to a weighted amount of graphite powder for the preparation of homogenized and SNP modified carbon paste.

A portion of the resulting paste was packed into the end of a 3 mm (i.d.) glass tube. Electrical contact was established via a copper wire. The surface was smoothed on a weighing paper.

Bare CPE was prepared by following the procedure explained above, without the incorporation of SNP in the carbon paste matrix. Bare CPEs and SNP modified CPEs were pretreated prior to electrochemical scannings by applying +1.40 V for 60 s in ABS buffer without stirring.

2.3. Electrochemical detection procedure

Each electrochemical measurements were performed with freshly prepared SNP-CPE. All experiments were carried out at room temperature (25 °C) and were repeated at least three times. Average values of current signals were presented in the histograms with the error bars.

2.4. The electrochemical characterization of SNP modified CPE

2.4.1. Cyclic voltammetry (CV)

In order to characterize the electrochemical behaviour of SNP modified electrode, and to recognize the pretreatment effects, the CV technique was used. The pretreated and unpretreated SNP-CPEs were immersed into ABS solution. Then, CV conditions were as follows. Scan rate: 100 mV/s, potential range: between +1.3 V and −0.8 V.

2.4.2. Differential pulse voltammetry (DPV)

DPV measurements were performed for monitoring of the reduction signal of SnO_2 itself, in ABS by scanning between (+0.80 V) to (−0.1 V) potential range vs. Ag/AgCl reference electrode at the pulse amplitude, 50 mV and the scan rate, 30 mV/s.

2.4.3. Electrochemical impedance spectroscopy (EIS)

The EIS measurements were performed in the presence of 2.5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) mixture as a redox probe prepared in 0.1 M KCl.

The impedance was measured in the frequency range from 100 mHz to 100 KHz at open circuit potential of +0.23 V vs. Ag/AgCl (sat. KCl), with a voltage amplitude of 10 mV. The frequency interval divided into 98 logarithmically equidistant measure points. The respective semicircle diameter corresponds to the charge-transfer resistance, R_{ct}, the values of which are calculated using the fitting programme supplied with AUTOLAB 302—FRA 2.0 module.

2.5. Electrochemical detection of adenine using CPE and SNP modified CPE by DPV

40 μL of 20 ppm adenine solution was dropped onto the surface of pretreated SNP-CPEs, dried in air for 30 min and then rinsed using ABS for 5 s.

For electrochemical detection of adenine oxidation signal, DPV measurements were performed in ABS by scanning in the potential range from (+0.2 V) to (+1.45 V) vs. Ag/AgCl reference electrode at the pulse amplitude, 50 mV with the scan rate, 30 mV/s.

The same experimental procedure was repeated using unmodified CPEs and the voltammetric transductions were accordingly performed.

3. Results and discussion

Fig. 1 displays the cyclic voltammograms obtained by (a) bare CPE and (b) CPE containing 40% SnO_2 nanoparticles (SNP) that were presenting the effect of pretreatment procedure. In the absence of pretreatment, the reduction signal of SnO_2 was measured at +0.299 V (shown in Fig. 1A-b) with a magnitude of 11.5 μA with RSD % ($n = 3$); 6.01%. After electrochemical pretreatment procedure at SNP modified CPE, the peak potential of SnO_2 reduction signal was shifted more negatively to +0.174 V (shown in Fig. 1B-b) with a higher signal as 27. 0 μA with RSD % ($n = 3$); 12.4.

The effect of scan rate on the reduction signal of SnO_2 was also checked by applying different scan rates; 25 mV/s, 50 mV/s and 100 mV/s in combination with CV technique (not shown). The optimum scan rate was chosen as 100 mV/s due to resulting in a better reproducibility.

Next, the electrochemical behaviour of CPE modified with SnO_2 nanoparticles (SNP) in different percentages was explored. The reduction signals of SNP were recorded, and the results were presented in Fig. 2. It was found that the signal of SNP was increased firstly gradually, and then sharply from 5% to 40%. After this amount, the signal decreased till 50%. The optimum amount of nanoparticles was chosen as 40% for development of SNP modified electrochemical sensor in our study.

Electrochemical impedance spectroscopy (EIS), which can be used as an effective and rapid method to measure the impedance value of the electrode surface during the process of the frequency variation [25], was used to differentiate the modification of nanoparticles into the carbon paste matrix of electrochemical sensor. The semicircle portion at higher frequencies correspond to the charge-transfer limited process and linear portion seen at lower frequencies may be ascribed to the diffusion process in the Nyquist plot of impedance spectra [26]. The diameter of the semicircle represents the charge-transfer resistance (R_{ct}) at the electrode surface [27]. Fig. 3A shows the impedance spectra obtained by bare CPE and SNP modified CPE in the absence/presence of pretreatment step. There was a decrease obtained at the R_{ct} values after pretreatment