



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 SnO₂ 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.

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1. Introduction

Tin dioxide (SnO₂) is a material with versatile applicability in a large number of physicochemical procedures. Thin films composed by SnO₂ 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, SnO₂ 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 SnO₂ 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 sim-

ple 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 nanobio-composite 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 SnO₂/gelatin composite film was studied by Jai et al. [13]. The nanocrystalline SnO₂ 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].

SnO₂ 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 SnO₂ 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 $\mu\text{g/mL}$ 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 thorough 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 $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ (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

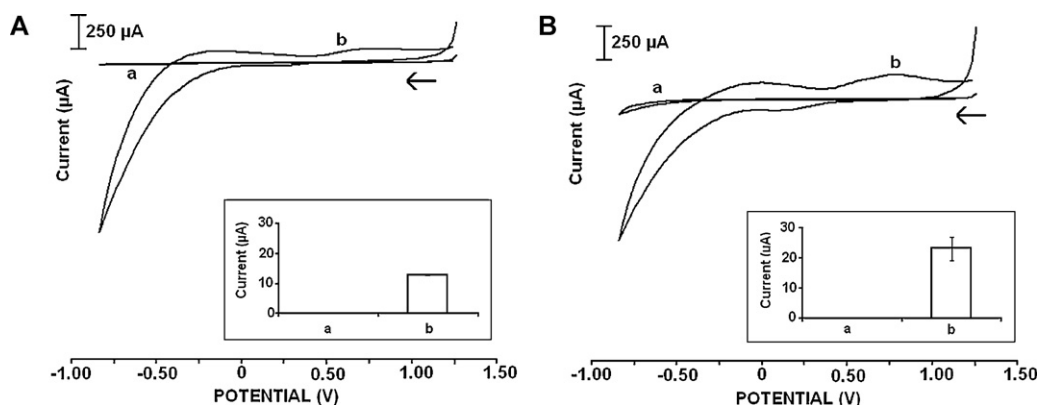


Fig. 1. Cyclic voltammograms representing the electrochemical behaviour of (a) bare CPE and (b) CPE containing 40% SnO₂ nanoparticles (SNP) by using (A) unpretreated and (B) pretreated electrodes ($n = 3$). CV conditions; 100 mV/s scan rate in potential range between +1.2 V and –0.5 V.

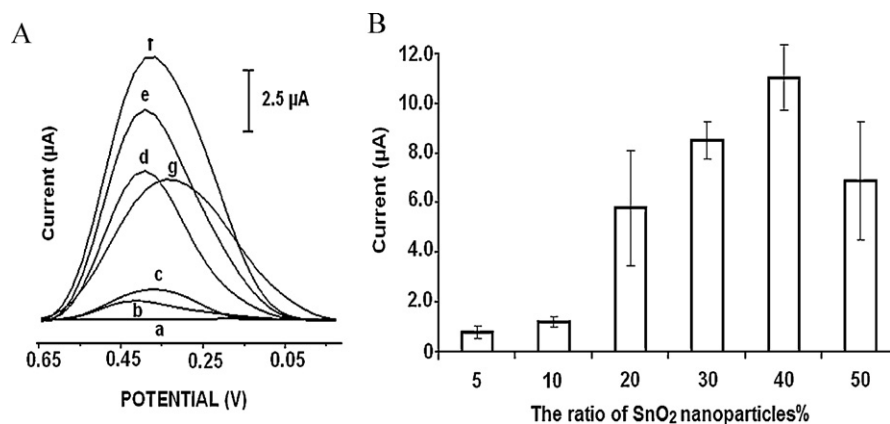


Fig. 2. (A) DPVs and (B) histograms representing the reduction signals of SnO₂ ($n = 5$) using CPE containing different SNP percentages: (a) 0%, (b) 5%, (c) 10%, (d) 20%, (e) 30% (f) 40% and (g) 50%. DPV conditions; the pulse amplitude; 50 mV and the scan rate; 30 mV/s in potential range between +0.8 V and –0.1 V by using the pretreated electrodes.

of the surfaces of CPE and SNP-CPE. It is obvious that the enhanced resistance to the charge-transfer occurred at the unpretreated surfaces of CPE and SNP-CPE.

In comparison to the R_{ct} value obtained by pretreated CPE (shown in Fig. 3B-c), an increase at the R_{ct} value was measured by pretreated SNP-CPE (Fig. 3B-d), and it has been a strong verification that SnO₂ nanoparticles had been placed properly in the carbon paste matrix. The larger R_{ct} value as two and half-folds can be explained that SnO₂ prevented redox couple, [Fe(CN)₆]^{3–/4–} from reaching the electrode surface, similarly observed in the earlier studies presented the carbon nanotubes modified disposable graphite electrodes [22] and polymer modified ones [28].

Fig. 4 shows the adenine oxidation signals measured by CPEs and SNP modified CPEs. The oxidation peak of adenine was observed at +1.092 V with the average magnitude of 4.2 μA with RSD % ($n = 3$); 32.1% for CPE, and +1.117 V with the average magnitude of 12.6 μA with RSD % ($n = 3$); 10.5% for SNP modified CPE. There was an increase about three times at the adenine signal contrast to the one measured by CPE in the absence of SnO₂ nanoparticle due to the fact that the improved surface area may yield an enhanced response of SNP modified CPE with a better reproducibility, similarly to the earlier study performed by SnO₂ nanoparticle modified graphite electrode for DNA analysis [29].

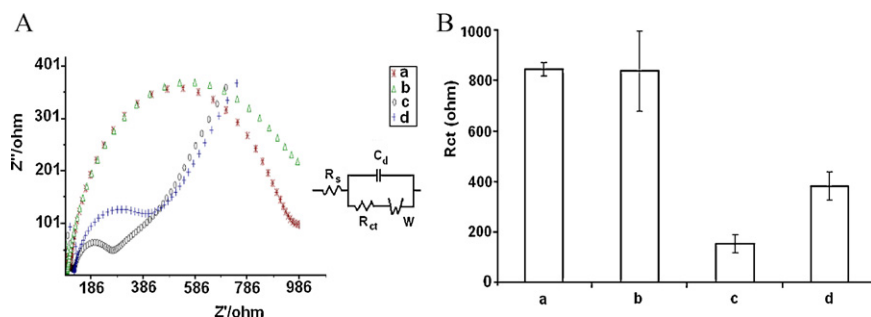


Fig. 3. (A) Nyquist diagrams recorded at CPE and SNP modified CPE before/after pretreatment step. Supporting electrolyte solution is 2.5 mM K₄[Fe(CN)₆]/K₃[Fe(CN)₆] (1:1) containing 0.1 M KCl. Inset was the equivalent circuit model used to fit the impedance data, the parameters of which are listed in the text; R_s is the solution resistance. The constant phase element C_d is then related to the space charge capacitance at the SnO₂/electrolyte interface. R_{ct} is related to the charge transfer resistance at the SnO₂/electrolyte interface. The constant phase element W is the Warburg impedance due to mass transfer to the electrode surface. (B) Histograms representing the R_{ct} values measured using (a) unpretreated CPE, (b) unpretreated SNP modified CPE, (c) pretreated CPE, and (d) pretreated SNP modified CPE.

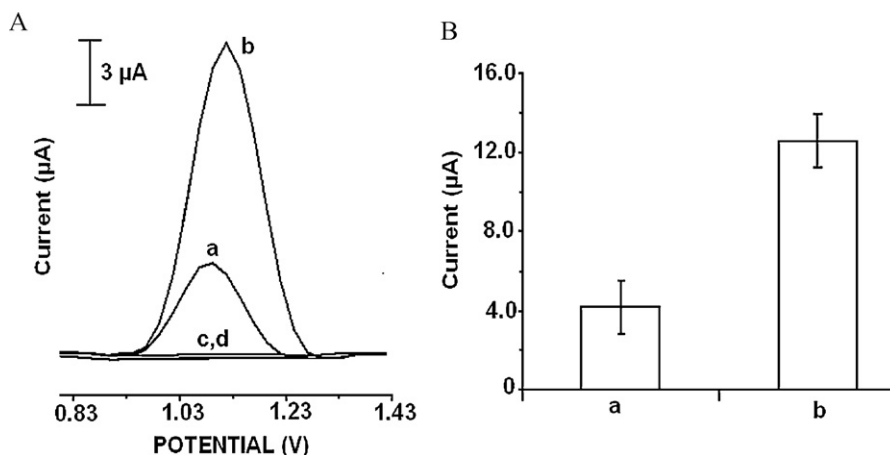


Fig. 4. (A) DPVs and (B) histograms presenting the adenine oxidation signals ($n=3$) obtained at bare CPE (a) and SNP modified CPE (b), and the blank signals at bare CPE (c) and SNP modified CPE (d) measured in the absence of adenine.

In our study, the SnO_2 nanoparticles were in a much smaller size that can increase the electrode surface resulting with more binding area for biomolecules in contrast to the nanomaterials based on tin oxide presented in the earlier studies of Topoglidis et al. [14] and Wang et al. [30]. In aspects of modified sensor preparation, these SNPs were mixed herein directly with a graphite powder as a part of carbon paste matrix, not using any time consuming surface chemistry process; e.g. a sol–gel procedure [14], or drying the nanocomposite film for overnight [23], or the thermal decomposition technique [31].

4. Conclusions

3–4 nm size of SnO_2 nanoparticles (SNPs) were used in this study for development of electrochemical biosensor. The electrochemical behaviour of SNP modified CPE was investigated in contrast to bare CPE by using voltammetric methods and electrochemical impedance spectroscopy. These SnO_2 nanoparticles were in a much smaller size in contrast to the nanomaterials based on tin oxide presented in the studies of Topoglidis et al. [14] and Wang et al. [30]. Besides, these SNPs were mixed herein directly with a graphite powder as a part of carbon paste matrix, not using any time consuming surface chemistry process; e.g. a sol–gel procedure [14], or drying the nanocomposite film for overnight [23], or the thermal decomposition technique [31].

The coupling of these nanoparticles combined with graphite sensor technology may bring some important advantages; such as, an enhanced response for DNA base, adenine. In addition, it also can eliminate the advanced surface modification, or regeneration schemes by resulting in a greatly simplified protocol for biosensor development. On going experiments have still been under progress in our laboratory for their further applications in order to detect specific nucleic acid hybridization, and also monitoring of some proteins.

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