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Electrochemical detection of toxic ractopamine and salbutamol in pig meat and human urine samples by using poly taurine/zirconia nanoparticles modified electrodes

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ABSTRACT

Detection of ractopamine and salbutamol has been developed by employing the facile synthesis of poly taurine/zirconia nanoparticles (ZrO_2) modified film glassy carbon electrode. The poly taurine/ZrO_2 nanoparticles were directly utilized for the detection of ractopamine and salbutamol using linear sweep voltammetry (LSV). The modified electrode successfully shows the oxidation peak for ractopamine adsorption at 0.65 V and salbutamol at 0.71 V, which is purely based on the detection of adsorption signals of ractopamine and salbutamol, at the electrode surface. Furthermore, the electrochemical measurements and surface morphology were studied using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) analysis. The modified electrode successfully detects the oxidation signals of ractopamine in the linear range of 1–28 μM and salbutamol in the linear range of 5–220 μM in laboratory samples. The proposed film also successfully detects the ractopamine signal (1–26 μM) in pig meat samples and salbutamol signal (1–114 μM) in human urine samples. It also exhibits two well-separated anodic oxidation peaks for uric acid and salbutamol in salbutamol-spiked human urine samples.

1. Introduction

Salbutamol and ractopamine (Scheme 1) are belongs to the general class of β_2-adrenergic agonists, and they were originally developed for the treatment of pulmonary disease, asthma and also could improve growth rate and reduce carcass fat when fed to animals [1]. However, β-agonists accumulated in animal tissues can cause acute poisoning when consumed by humans, with symptoms of muscular tremor, cardiac palpitation, nervousness, headache, muscular pain, dizziness, nausea, vomiting, fever, and chills [2,3]. Therefore the use of these compounds has been banned in most countries.

Up to now, various analytical methods have been developed in an effort to combat the illicit usage of β-agonists and related compounds in animal tissues and feeds. These methods include liquid chromatography with mass spectrometric or electrochemical detection [5], gas chromatography with mass spectrometry [6,7], and enzyme-linked immunoassay with polyclonal or monoclonal antibodies [8]. Recently, electrochemical methods are found to be convenient, reliable and important for the detection of β_2 agonists, because they can be oxidized at bare or modified electrodes. However, electrochemical methods are low cost and fast analysis. Various types of modified electrodes are used for the detection of these compounds such as, carbon nanotube modified electrode [9,10], fullerene modified electrodes [11] imprinted polymer modified electrodes [12] and graphene modified electrodes [13]. Thus, broad-spectrum detection methods are urgently needed for quick screening of various types of β-agonists and their analogs that may exist in animal feeds, and urine samples.

In recent years studies of nanoparticles and organized low-dimensional nanostructures have their unique capabilities to enhance mass transport, facilitate catalysis, increase surface area, and control an electrode's microenvironment [14]. Also, the nanoparticles provide a high surface-to-volume ratio and enhance the electron transfer kinetics [15]. ZrO_2 nanoparticles are an inorganic oxide, which have been demonstrated as an ideal material for the immobilization of biomolecules with oxygen groups because of its thermal stability, chemical inertness, lack of toxicity, and affinity for the groups containing oxygen [16]. The nanoparticles also provided a three-dimensional stage, and some of the restricted orientations also favored the direct electron transfer between the protein molecules and the conductor surface [17]. Taurine is a well-known dissociated amino acid, which exhibits important physiological functions and pharmacological characteristics. It has

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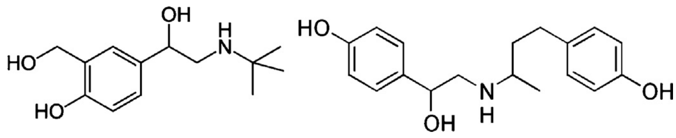

Scheme 1. Chemical structure of salbutamol and ractopamine.

widely been used as food nutrition enhancer and common drug [18]. Hence, in this report we have particularly focused to develop an electrochemical sensor for the detection of salbutamol and ractopamine in pig meat and human urine samples by using poly taurine/ZrO_2 nanoparticles modified electrodes. The modified electrodes have been fabricated on GCE and ITO electrodes by cyclic voltammetry (CV). Electrochemical characterization and surface analysis of the film were carried out using CV, EIS and SEM techniques. Further this electrode shows the good detection signals for the salbutamol and ractopamine in both lab and real samples, respectively.

2. Experimental

2.1. Apparatus

Electrochemical measurements like cyclic voltammetry (CV) and linear sweep voltammetry were performed by a CHI 1205 A electrochemical analyzer. A conventional three-electrode cell were used at room temperature with glassy carbon electrode (GCE) (surface area = 0.07 cm^2) as the working electrode, Ag/AgCl (saturated KCl) electrode as reference electrode and a platinum wire as counter electrode. The potentials mentioned in all experimental results were referred to standard Ag/AgCl (saturated KCl) reference electrode. Surface morphology of the film was studied by SEM (Hitachi, Japan). Electrochemical impedance studies (EIS) were performed by using ZAHNER impedance analyzer (ZAHNER Elektrik Gmbh & Co. KG, Germany).

2.2. Materials

Zirconyl chloride octahydrate, taurine, ractopamine and salbutamol were purchased from Sigma–Aldrich. Freshly prepared salbutamol and ractopamine solutions prepared every day. The other chemicals (Merck) that are used in this investigation were of analytical grade (99%). Pork meat was purchased from nearby supermarket and the ventolin tablets (salbutamol) were purchased from near drug store. All the solutions are prepared using double distilled water. Electrocatalytic studies were carried out in 0.05 M pH 7 PBS. Pure nitrogen gas was passed through all the experimental solutions for removing dissolved oxygen.

2.3. Preparation of poly taurine/ZrO_2 nanocomposite modified electrode

Prior to the electrodeposition process, the bare glassy carbon electrode was initially polished with 0.05 μM alumina powder on BAS polishing pad and ultrasonically cleaned in water for a minute. The electrode was then successfully washed with double distilled water and used. The glassy carbon electrode was modified by co-electrochemical deposition of zirconia nanoparticles (2 mM) and taurine (2 mM) in pH 7 solution, with a potential scan between −1.5 and 2 V at the scan of 0.02 V s^{-1} for 10 cycles. Here, the equivalent molar concentrations (2 mM) of taurine and zirconia precursor have been taken for the balanced deposition of both poly taurine/ZrO_2 nanocomposites. The modified electrode was then rinsed with double distilled water and used for further electrochemical studies.

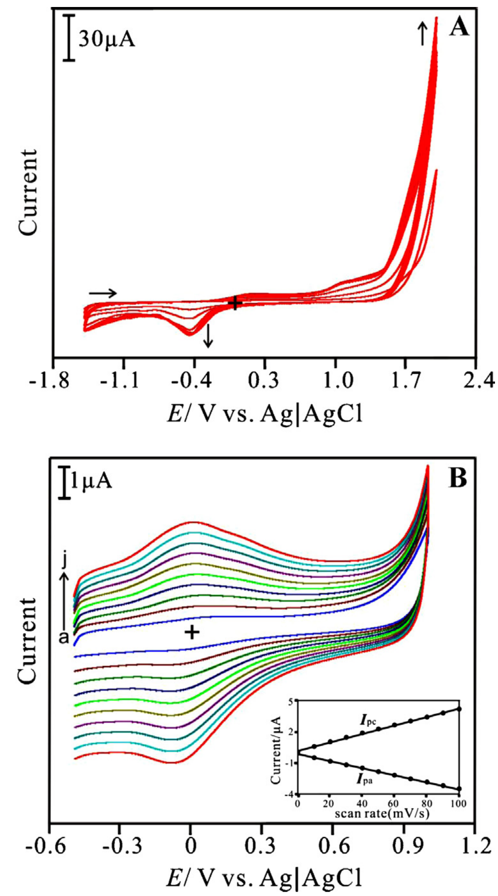

Fig. 1. (A) Cyclic voltammogram of poly taurine/ZrO_2 nanocomposite film electrodeposited on the GCE from 0.05 M pH 7 PBS containing $ZrOCl_2$ (2×10^{-3} M) and taurine (2×10^{-3} M) and potential scan between −1.5 and 2 V for 10 cycles at the scan rate of 0.02 V s^{-1}. (B) Different scan of the poly taurine/ZrO_2 nanocomposite film modified electrode in pH 7 at scan rate varies from 0.01, 0.02, 0.03, 0.04,0.05, 0.06, 0.07, 0.08, 0.09, 0.1 V s^{-1}. Inset shows a current vs. scan rate plot at pH 7.

3. Results and Discussion

3.1. Electrochemical characterization of poly taurine/ZrO_2 nanocomposite film modified GCE

Fig. 1A shows the electrochemical deposition of poly taurine/ZrO_2 nanocomposite film on GCE. Cyclic voltammogram were recorded by continuous potential cycling for 10 cycles in the range of −1.5 to 2 V vs. Ag/AgCl (sat KCl) at a scan rate of 0.02 V s^{-1} in 0.05 M pH 7 PBS containing 2 mM taurine and $ZrOCl_2$. Taurine monomer oxidation occurs at a more positive oxidation potential of 1.7 V and possess a small peak at 0.16 V shown for the deposition of poly taurine [19]. In the reverse the scan the peak appears at −0.4 V results the presence of zirconia nanoparticles [20]. A continuous increase in scan cycle numbers the anodic and cathodic peak potentials shifted toward the positive and negative directions. The shifts are possibly related to change in resistance of the electrode during polymerization. Based on this result we conclude that the co-electrodeposition of poly taurine occurs with the zirconia nanoparticles and exhibits as a thin layer on the electrode surface respectively.

In the next step the poly taurine/ZrO_2 nanocomposite electrode was employed for the different scan rate studies in pH 7 PBS. Fig. 1B shows the different scan rate studies of the poly taurine/ZrO_2 nanocomposite film modified GCE. Here all the anodic and cathodic peak currents of the nanocomposite film increases linear with