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A novel voltammetric sensor based on carbon nanotubes and nanoparticles of antimony tin oxide for the determination of ractopamine

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ABSTRACT

An electrochemical sensor was prepared by the modification of a glassy carbon electrode (GCE) with carbon nanotubes (CNTs) and nanoparticles of antimony tin oxide (ATO). The surface layer was characterized by scanning electron microscopy (SEM), energy dispersive X-ray diffraction method (EDX) and ATR FT-IR spectroscopy. The proposed electrode was assessed in respect to the electro-oxidation of ractopamine. Compared with a bare GCE and a GCE electrode modified with CNTs, the ATONPs/CNTs/GCE exhibited a great catalytic activity towards the oxidation of ractopamine with a well-defined anodic peak at 600 mV. The current response was linear with the concentration of ractopamine over the range from 10 to 240 nM with a detection limit of 3.3 nM. The proposed electrode enabled the selective determination of ractopamine in the presence of high concentrations of ascorbic acid (AA), dopamine (DA) and uric acid (UA). The proposed electrode was successfully applied for the determination of ractopamine in feed and urine samples. The sensitive and selective determination of ractopamine makes the developed method of great interest for monitoring its therapeutic use and doping control purposes.

1. Introduction

Ractopamine, a beta-adrenergic agonist drug, is used to improve weight gain, carcass leanness and feed efficiency in livestock by diverting nutrients from fat deposition to muscle tissue production [1–4]. However, ractopamine is prohibited in horse racing because of its abuse as a stimulant. It has also been banned as a feed additive due to potential risks to the cardiovascular and central nervous systems [4–6]. Thus, the determination of ractopamine is important for both monitoring its therapeutic use and doping cases of horses in competitions. A number of analytical methods have been applied for the determination of ractopamine in samples including immunoassay [7,8], GC–MS [9], LC–MS [10,11], HPLC [12,13], fluorescence spectroscopy [14,15], electrophoresis [16], chemiluminescence [17,18] and voltammetric methods [19–23]. However, some of the above techniques are expensive and require time-consuming steps. Electrochemical sensors have widely been used in electroanalysis due to their unique physical and chemical properties such as excellent electrocatalytic activity, good conductivity and high mechanical strength [24–29]. Furthermore, CNTs and nanoparticle modified electrodes showed great performances in terms of increased sensitivity, mass transport, resistance to surface fouling, decreased overpotential and low detection limit [30–37]. Nanoparticles of metal oxides have several advantages including excellent electrocatalytic activity, increased current response and improved voltammetric behaviour [38,39]. A recent study has indicated that the conductivity and sensitivity increased as antimony was doped into a layer of tin oxide [40]. The nanomaterial based sensors provide highly selective and sensitive approach to the analysis of a wide range of drugs since the electrode materials play a critical role in the construction of high-performance sensing platforms for the determination of drug molecules through various analytical principles [41,42]. Furthermore, functional nanomaterials cannot only produce a synergic effect to accelerate the signal transduction but also amplify biorecognition events for drug sensing [43]. For example, the selectivity is sometimes limited at conventional electrodes due to the interference from the other redox active molecules such as ascorbic acid (AA) and uric acid (UA) which may undergo oxidation at similar potentials to the target drug molecule in biological samples [44–46]. The most important method to overcome such problems is to modify the conventional electrodes with nanomaterials which alter the electrode kinetics of species so that the oxidation potential of the target drug becomes shifted from that required to oxidize the interfering molecules [46–48]. In this study, a novel composite electrode based on carbon nanotubes and nanoparticles of antimony tin oxide has been prepared for the voltammetric determination of ractopamine. The proposed voltammetric sensor exhibited strong catalytic activity towards the oxidation of ractopamine. It also provided a very suitable and effective procedure for the sensitive and selective determination of ractopamine as the modification of GCEs with CNTs and nanoparticles of ATO improved peak separation from interfering compounds such as AA, DA and UA, and improved the detection limit.

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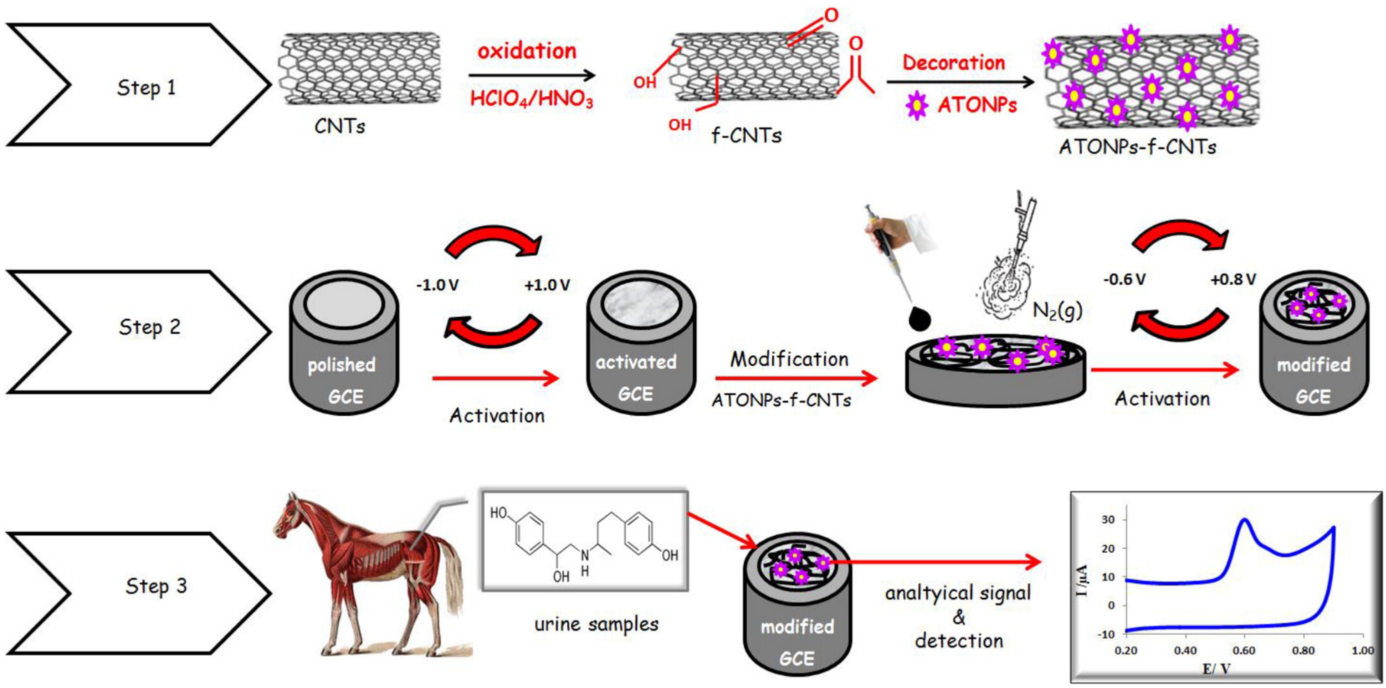

Scheme 1. A schematic illustration of the proposed electrode.

2. Experimental

2.1. Chemicals

Ractopamine, AA, DA and UA were obtained from Sigma-Aldrich (St Louis, USA). Chloroform was purchased from Merck (Darmstadt, Germany). Carbon nanotubes (CNTs) and antimony tin oxide nanoparticles were obtained from US-Nano, USA. Stock solutions were prepared with 0.1 M phosphate buffer at pH 7.0. Ultrapure water was used for the preparation of solutions. Solutions were deoxygenated by purging nitrogen prior to measurements.

2.2. Apparatus

An Autolab potentiostat (Ecochemie, The Netherlands) was used for voltammetric measurements. A three-electrode system was used: a glassy carbon electrode as working electrode [3 mm in diameter (BASi, USA)], a Pt wire counter electrode and a Ag/AgCl reference electrode.

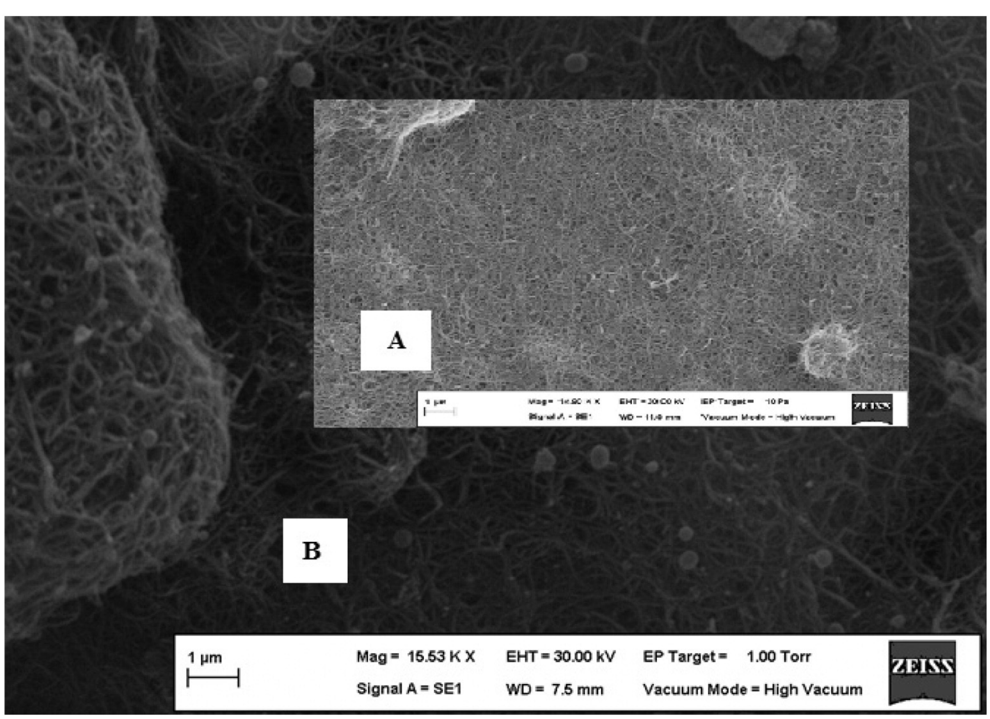

Fig. 1. SEM images of CNTs/GCE (A) and ATONPs/CNTs/GCE (B).