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Decorating carbon nanotubes with nanoparticles of indium tin oxide for the voltammetric determination of metaproterenol

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ABSTRACT

A voltammetric sensor prepared using a composite of multi-walled carbon nanotubes (MWCNTs) and indium tin oxide nanoparticles (ITONPs) were applied for quantifying metaproterenol in pharmaceuticals and urine samples. The characterization of the composite layer was performed using energy dispersive X-ray and scanning electron microscopic techniques. ITONPs/MWCNTs/GCE exhibited a great electrocatalytic effect towards the oxidation of metaproterenol with a well-defined peak at 550 mV. Compared with a number of electrodes, a GCE decorated with both MWCNTs and ITO nanoparticles also exhibited a large enhancement of voltammetric response for metaproterenol. In addition, the higher concentration of uric acid (UA) does not interfere with the selective quantification of metaproterenol. Differential pulse voltammetry (DPV) was performed for the determination of metaproterenol at ITONPs/MWCNTs/GCE. A linear plot yielding a detection limit of 1.2×10^{-8} M was obtained for current responses of metaproterenol against concentrations in the range of 3.0×10^{-8}–2.2×10^{-5} M. The proposed modified electrode provided better voltammetric behavior, good reproducibility and long-time stability. The selective quantification of metaproterenol makes the proposed electrode of great interest for both monitoring its therapeutic use and for doping analysis.

1. Introduction

Metaproterenol, a beta-adrenergic agonist drug, relaxes the smooth muscle in the airways, allows air to flow in and out of the lungs more easily [1]. It is taken due to its anabolic effects such as decreasing deposition of fat and increasing lean of the muscle [2]. However, metaproterenol has been banned in competitions because of being abuse as a stimulant [3]. In addition, the consumption of metaproterenol may cause a serious effect to human health due to its slow metabolism and the long half-life [4]. Thus, a selective quantification of metaproterenol is of great importance to monitor its therapeutic use and control its abuse in sports.

A limited number of analytical techniques were utilized for quantifying metaproterenol in samples including HPLC [5], GC–MS [6], chemiluminescence [7–9] and Raman spectrometry [10]. However, these techniques require time-consuming steps and also the sample pretreatment and high costs make them unsuitable for the routine analysis of samples. Meanwhile, voltammetric techniques provide high sensitivity and rapidness to the quantification of drugs [11–14]. A few electrodes were reported for the quantification of metaproterenol including carbon nanotubes modified GCE [15] and gold nanoparticles modified GCE [16]. Electrodes modified with MWCNTs showed great performances such as response time, increased sensitivity, resistance to surface fouling, decreased overpotential and limit of detection [15].

In addition, nanoparticles can display several advantages when used in electroanalysis: enhancement of mass transport, catalysis and high effective surface area [16]. Composite electrodes prepared with MWCNTs and nanoparticles have presented several advantages such as excellent catalytic activity, long-term stability and lower limit of detection [17–22]. It has recently been reported that the electrocatalytic activity increased using a glass plate modified with indium tin oxide [23].

In this paper, we report the quantification of metaproterenol in pharmaceuticals and urine samples using a MWCNT modified GCE decorated with nanoparticles of indium tin oxide. The experimental data showed that modifying GCEs with ITO nanoparticles and MWCNTs presented great electrocatalytic activity, high stability and excellent reproducibility for the oxidation of metaproterenol.

2. Experimental

2.1. Chemical reagents

Uric acid (UA) and metaproterenol (MP) were obtained from Sigma-Aldrich. Chloroform was purchased from Merck. MWCNTs and ITO nanoparticles were obtained from US-Nano, USA. Solutions of metaproterenol and uric acid were prepared with 0.1 M PBS at pH 8.0. Ultra-pure water was used for the preparation of solutions. Solutions were deoxygenated by purging nitrogen before running experiments.

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2.2. Instrumentation

An Autolab potentiostat (EcoChemie) was utilized for electrochemical experiments. A three-electrode system was used: a GCE as working electrode [3.0 mm in diameter (Bioanalytical Systems, USA)], a Pt wire counter electrode and a Ag/AgCl reference electrode (Metrohm, Switzerland).

2.3. Preparation of the modified electrodes

Working electrodes were polished with 1 μm and 0.3 μm alumina powder. They were then sonicated for 5 min in ethanol and rinsed with ultrapure water. Afterwards, cyclic voltammetry was performed in 0.1 M PBS at pH 7.0 over the potential range from −1.0 to +1.0 V at a scan rate of 100 mV/s to activate the glassy carbon electrodes. Prior to the modification, MWCNTs were functionalized in a mixture of concentrated perchloric acid and nitric acid for 5 h in an ultrasonic bath in order to increase the conductivity and therefore the sensitivity of the layer. Functionalized MWCNTs were then filtered, washed with water and dried in air. 1 mg of functionalized MWCNTs and 0.1 mg of nanoparticles of ITO (In_2O_3: 90 wt.% + SnO_2: 10 wt.%) were dispersed in 5 ml of chloroform and sonicated in an ultrasonic bath for 30 min. 5 μL of the suspension was cast on the electrode surface and then chloroform allowed to evaporate. Then, the resulting electrode (ITONPs/MWCNTs/GCE) was reactivated in 0.1 M PBS at pH 8.0 by CV in the potential range between −0.6 and +0.8 V at 100 mV/s. A schematic illustration of the preparation of the proposed electrode is given in Scheme 1. The experimental results showed an optimal ratio of 10:1 for the mixture of MWCNTs and ITO nanoparticles. Furthermore, the amount of composite layer on the electrode surface should be 5 μL in order to obtain an improvement in the voltammetric response for metaproterenol. The results have shown that greater amounts of the composite mixture resulted in remarkable decreases in the sensitivity and reproducibility.

3. Results and discussion

3.1. Characterization of surface

The surface material was characterized by SEM. An image for the layer of MWCNTs is shown in Fig. 1a. No aggregation was observed for the layer of MWCNTs. This indicated the MWCNTs were dispersed homogeneously on GCE. As seen in Fig. 1b, ITO nanoparticles are distributed on MWCNTs. The average size of nanoparticles was ca. 115 nm. The EDX results also exhibited that In, Sn, O, C, Pd and Au were on the surface (Fig. S1 in Supplement information). However, Pd and Au were obtained from the palladium–gold coatings of the electrode during SEM analysis.

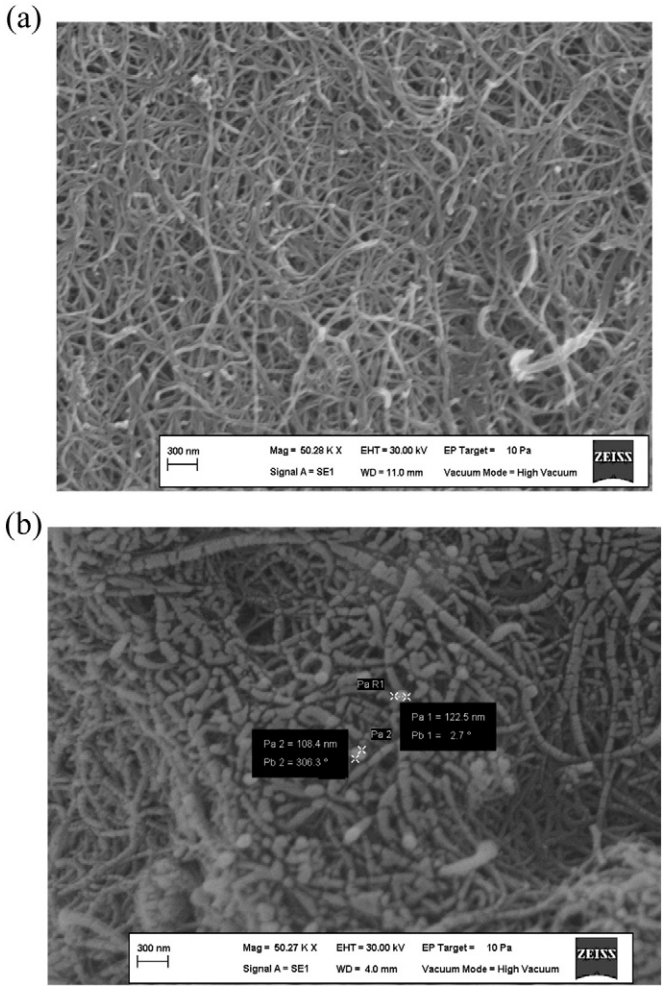
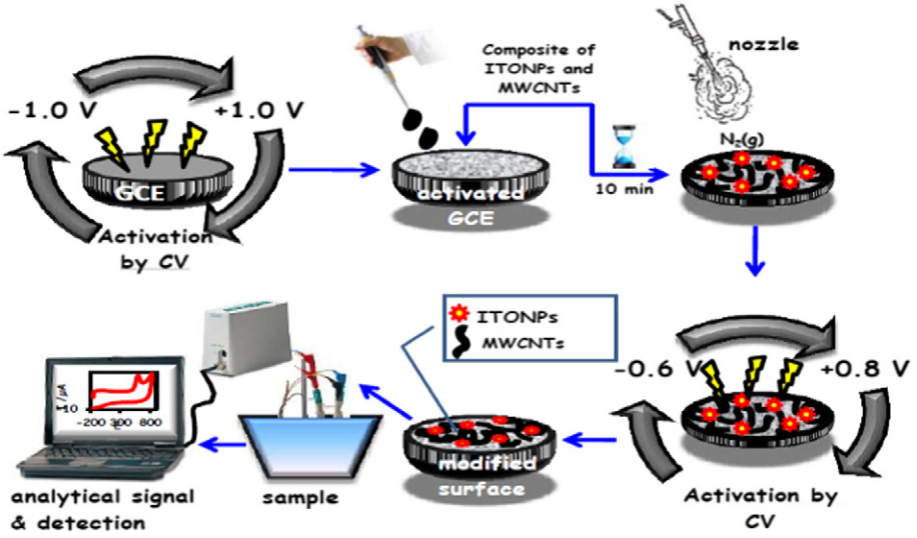


Fig. 1. SEM images of MWCNTs/GCE (a) and ITONPs/MWCNTs/GCE (b).



Scheme 1. An illustration of the preparation of the proposed electrode.