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Cobalt oxide acicular nanorods with high sensitivity for the non-enzymatic detection of glucose

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ABSTRACT

Acicular cobalt oxide nanorods (CoONRs) were prepared for the non-enzymatic detection of glucose, first by directly growing layered cobalt carbonate hydroxide (LCCH) on a conducting fluorine-doped tin oxide (FTO) substrate using a simple chemical bath deposition (CBD) technique and then by transforming the LCCH into CoONRs through pyrolysis. The composition and grain size of the films of LCCH and CoONRs were verified by X-ray diffraction (XRD); their morphologies were examined by scanning electron microscopic (SEM) and transmission electron microscopic (TEM) images. CoONRs showed high electrocatalytic activity for the electro-oxidation of glucose in alkaline media, and the activity was strongly influenced by NaOH concentration, annealing temperature of CoONRs, and thickness of CoONRs film. The pertinent sensor could be successfully used for the quantification of glucose by amperometric method. The sensing parameters include wide linear range up to 3.5 mM, a high sensitivity of 571.8 μA/(cm^2 mM), and a remarkable low detection limit of 0.058 μM. The CoONRs modified electrode exhibited a high selectivity for glucose in human serum, against ascorbic acid, uric acid, and acetaminophen.

1. Introduction

Diabetes mellitus is a worldwide public health problem. This metabolic disorder results from insulin deficiency and hyperglycemia and is reflected by blood glucose concentrations higher or lower than the normal range of 80–120 mg/dL (Wang, 2008); the diagnosis and management of diabetes mellitus requires a tight monitoring of blood glucose levels. Millions of diabetics test their blood glucose levels daily, making glucose the most commonly tested analyte. This situation led to crucial and fascinating research on the detection of glucose. There has been a great deal of research activities on the detection of glucose, ever since Clark and Lyons firstly reported a glucose biosensor by encapsulating glucose oxidase within polyethylene on the metal electrodes (Clark and Lyons, 1962). An electrochemical glucose biosensor was developed as early as in 1967 (Updike and Hicks, 1967); this was an enzyme electrode and had a glucose oxidase (GOx) immobilized on a gel to measure the concentration of glucose in biological solutions and in the tissues *in vitro*. This development by Updike and Hicks has triggered great research activities in favor of enzyme based glucose biosensors (Wilson and Turner, 1992; Yao, 1983; Yang et al., 2002; Wang et al., 2003). The detection of glucose by an enzyme based biosensor can be accomplished by measuring the anodic current of the electro-oxidation of H_2O_2, which is the by-product of the reaction between GOx(FAD) and glucose (Wang, 2008). However, for an enzyme-type biosensor, the by-product, H_2O_2 has a high sensing potential of 0.6 V vs. Ag/AgCl/sat'd KCl, and this high sensing potential causes large interference noises. In other words, there are some species, e.g., ascorbic acid (AA) and uric acid (UA) in the case of blood serum (Wang, 2008), that can undergo oxidation within this potential and thereby cause unnecessary amperometric sensing signals; this is a major problem especially with regard to an electrochemical sensing. In addition, the issue of instability of GOx also has to be addressed, because the enzymatic glucose biosensors lack stability due to the nature of enzyme.

To solve the above-mentioned problems, some types of non-enzymatic glucose sensors have been investigated and developed. In recent years, several kinds of metal oxides, e.g., CuO (Reitz et al., 2008; Zhuang et al., 2008; Wang et al., 2009; Jiang and Zhang, 2010), MnO_2 (Chen et al., 2008), NiO_x (Zhang et al., 2010; Liu et al., 2009; Lu et al., 2010), and CoO_x (Heli and Yadegari, 2010; Scavetta et al., 2010; Ding et al., 2010) have been extensively explored as the sensing materials for developing non-enzymatic glucose biosensors. Among them, CoO_x has received much attention due to its electro-catalytic properties and chemical stability. The only report for rather a comprehensive study on the sensor parameters of glucose by a type of CoO_x modified electrode is by Ding et al. (2010), whose electrode, however, is CoO_x nanofibers-Nafion®/glassy carbon electrode; these authors have obtained a cobalt oxide modified electrode by electrospinning cobalt oxide nanofibers-film on an

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aluminum foil, its subsequent calcination, and transfer to a glassy carbon electrode. It is very important to note that the ultimate electrode in their case was a Nafion® casted cobalt oxide glassy carbon electrode, and not a pure cobalt oxide modified electrode. As there is no other report on the use of pure (non-composite) cobalt oxide modified electrode for sensing glucose, we make here a brief comparison of the sensing performance of hitherto best CoO_x (Nafion®) modified electrode developed by Ding et al. (2010) with that of our CoO_x modified electrode. The sensitivity for the estimation of glucose sensor obtained by us is 571.8 $\mu A/(mM\,cm^2)$, which is 15 times higher than theirs' sensitivity (36.25). The detection limit is 0.058 μM in our case, which is over 10 times lower than their detection limit (0.97 μM). The linear range is up to 3.5 mM, which is also higher than their linear range (2.04 mM). The applied potential for sensing in our case is 0.50 V, which is lower than their applied potential (0.59 V); this implies, in our case, a reduction or nullification of the sensing signals from other interferences. In this work, pure Co_3O_4 was used as the coating material to detect glucose, and the interferences from UA and AA (in their physiological levels) were found to be negligible. However, in Ding's work, they had to introduce the Nafion® composite film to reduce the interference, and even with the Nafion® composite film, the interferences from AA and UA were still obvious (>10% for physiological levels).

In this study, we prepared a film of acicular cobalt oxide nanorods (CoONRs) on a conducting fluorine-doped tin oxide (FTO) electrode by using a simple chemical bath deposition (CBD) technique, and used the thus formed cobalt oxide electrode as a sensor for the detection of glucose; this approach has never been reported for a pure cobalt oxide electrode for the detection of glucose. The effects of NaOH concentration, annealing temperature of CoONRs, film thickness of CoONRs on glucose sensing were investigated, and these parameters were optimized. Amperometric detection of glucose was performed and pertinent interference study was made for AA, UA, and acetaminophen (AP). The proposed CoONRs modified electrode exhibits a high sensitivity, low detection limit, and high selectivity for glucose. The electrode was also verified to be suitable for the detection of glucose in human blood serum.

2. Experimental

2.1. Chemicals

Cobalt nitrate 6-hydrate (A.C.S. reagent, J.T. Baker), urea (98%, Sigma–Aldrich), and sodium hydroxide (puriss, Riedel-de Haën) were used as received. 50 mM of glucose sample solution was prepared before each experiment by direct dilution of D-(+)-glucose (99.5%, Sigma–Aldrich) in NaOH. The concentration of NaOH was optimized before glucose sensing. Ascorbic acid (>99%, Sigma), uric acid (>99%, Sigma), and acetaminophen (>99%, Sigma) were used for the interference test. Deionized water (DIW) was used throughout the work.

2.2. Apparatus

Cyclic voltammetry (CV) and amperometric experiments were performed with a CHI 440 electrochemical workstation (CH Instruments, Inc., USA), using a conventional three-electrode system. An FTO glass modified with cobalt oxide (CoONRs/FTO electrode) was used as the working electrode. A Pt foil (4.0 cm × 1.0 cm) and a Ag/AgCl/saturated KCl (homemade) were used as the counter and reference electrodes, respectively. All electrochemical experiments were performed at room temperature and all the potentials are reported against the Ag/AgCl/sat'd KCl reference electrode.

The nanostructure of cobalt oxide was observed by using scanning electron microscope (SEM, Nova NanoSEM 230). Transmission electron microscopy (TEM, Hitachi H-7100, Japan) was also used to obtain the image of cobalt oxide nanorods. The composition of the cobalt oxide thin film was verified by X-ray diffraction patterns (XRD, X-Pert, the Netherlands) with Cu Kα radiation. High-resolution transmission electron microscopy (HRTEM, Tecnai G2, 200 kV) was also employed to verify the crystalline composition of the nanostructure.

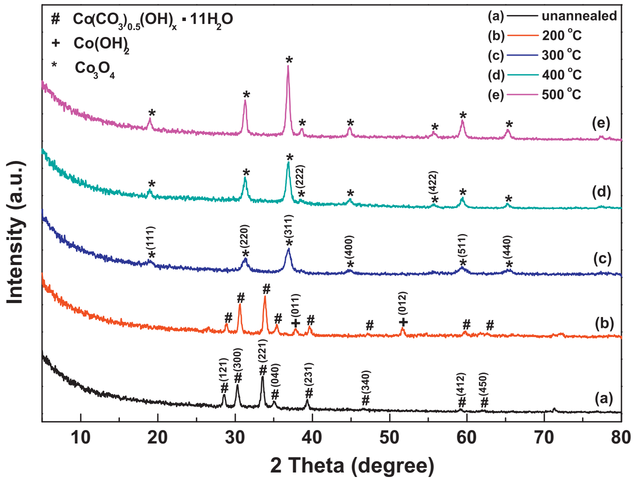

Fig. 1. XRD patterns of (a) the unannealed LCCH film, (b) the LCCH film annealed at 200 °C; (c), (d), and (e) are the XRD patterns of the CoONRs film annealed at 300 °C, 400 °C, and 500 °C, respectively.

2.3. Preparation of the CoONRs modified FTO electrode

The CoONRs modified electrode was prepared by depositing layered cobalt carbonate hydroxide (LCCH) on the FTO glass, using chemical bath deposition (CBD), followed by an annealing process to transform the LCCH to the cobalt oxide nanorods. In the CBD process, an FTO glass substrate (Solaronix SA, 15 Ω/□ with an exposed geometric area of 1.5 cm^2) was suspended upside-down in a closed bottle with an aqueous solution, containing 0.15 M of cobalt nitrate and 6.25 wt% of urea, at 90 °C for 4 h. After the CBD process, the modified FTO with LCCH was rinsed with deionized water and dried at room temperature. Thereafter, the LCCH on the FTO was converted to cobalt oxide by annealing it at 300 °C and up to 500 °C for 30 min in air. The concentration of urea in the bath solution was changed to obtain different film thicknesses, when necessary. Further, to obtain different compositions and grain sizes of the film, different annealing temperatures were employed.

2.4. Amperometric detection of glucose

For the detection of glucose by amperometry at a constant potential by using the CoONRs modified FTO electrode as the biosensor, a suitable sensing potential in the limiting current plateau region between 0.15 and 0.6 V was determined by applying linear sweep voltammetry (LSV) at a scan rate of 0.1 mV/s in 1.0 M bare NaOH solution and in the same solution containing 3.0 mM glucose. The current densities in the concentration range between 0.2 and 6.0 mM were collected and the calibration curve for glucose was constructed.

3. Results and discussion

3.1. Characterization of the films of LCCH and CoONRs

Fig. 1 shows the XRD pattern of the as-prepared film and its patterns after annealing it at four different temperatures. As