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RESEARCH PAPER

Relationship Between Surface Morphology and Performance of a Spirally Hierarchical Structure-based Electrochemical Glucose Sensor

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Abstract: A spirally hierarchical structure-based glucose enzymatic electrode was prepared in the experiment on the basis of that zinc oxide nanowires were hydrothermally synthesized on the surface of an Au cylindrical spiral formed by manually winding an Au fiber around an optical fiber core, and then glucose oxidase was immobilized on these nanowires by physical adsorption. The surface morphologies of the spirally hierarchical structures and corresponding enzymatic electrodes were extracted, and the electrochemical performances of the enzymatic electrodes were characterized. The results indicated that the synthesizing parameters of zinc oxide nanowires affected significantly the surface morphologies of the glucose oxidase immobilization on the spirally hierarchical structures, and the performances of related glucose sensors. As the Zn^{2+} concentration of growth solution was set at 25 mM, the surface morphology was determined as roughness to be 0.10 μm and correlation length 0.29 μm, resulting in a better immobilization of glucose oxidase upon zinc oxide nanowires. In this case, the sensitivity of the glucose sensor was determined to be 2.15 μA mM^{-1} cm^{-2}, the linear range was 0–4.50 mM, the low detection limit was 9.20 μM and Michaelis-Menten constant was 3.68 mM. The results not only benefited the batch production of the spirally hierarchical structure-based enzymatic electrodes, but also significantly improved the performances of the glucose sensors.

Key Words: Hierarchical structure; Surface morphology; Glucose biosensor; Cyclic voltammetry; Amperometric response

1 Introduction

Hierarchical electrochemical glucose sensors based on direct electron transmission between glucose oxidase (GOD) and working electrodes composed of a microscale substrate and a nanoscale matrix material were widely applied in medicine, biology, food industry and environmental monitoring domains[1–5]. Due to the large specific surface area, strong resistance to be oxidized, non-toxicity and excellent biocompatibility, zinc oxide (ZnO) nanowire was frequently employed as an ideal matrix material[6]. For bulk-production the hierarchical structure-based electrochemical glucose sensors, not only the synthesizing parameters need to be regulated, but also the surface morphologies and GOD immobilization quantitatively characterized.

Two kinds of microscale substrates were used to construct hierarchical structure-based electrochemical glucose sensors, such as planar (silicon or glass substrates with Au deposited, indium-tin-oxide glass)[7,8] and cylindrical (Au or Ag fiber, and glass carbon fiber) ones[9–11]. The surface areas of these substrates should be further increased. The specific surface area and the surface morphology of ZnO nanowire film affected significantly GOD immobilization, but the former was difficult to be determined[12], and the latter was directly characterized with scanning electron microscopy (SEM) whose measurement data was limited, the characterization parameters were insufficient, hence the evaluation results were incomplete[13,14]. Synthesizing parameters determine the

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surface morphology of a ZnO nanowire film, which leads to various GOD immobilizations, and thus eventually result in different performances of the glucose sensors as a batch. Therefore the quantitative relationship among these influencing factors needs to be thoroughly investigated.

On the basis of our previous work[15], in this work, a ZnO nanowire-based spirally hierarchical structure was proposed as a batch constructed. The surface morphologies of the working electrodes without and with GOD as well as the electrochemical performances of the enzymatic electrodes were quantitatively characterized. Brief quantitative relationship among synthesizing parameters, surface morphologies, GOD immobilization and the glucose sensor performances was established.

2 Experimental

2.1 Apparatus and reagents

BII-3 magnetic stirrer (Shanghai Sile Instrument Co., Ltd., China), DZF-6020 vacuum drier (Shanghai Hengyi Sci-Tech Co., Ltd., China), KQ3200DE ultrasonic washer (Shanghai Shengyan Ultrasonic Equipment Co., Ltd., China), SU-8000 Scanning electron microscope (Hitachi, Japan) and CHI660D electrochemical workstation (Shanghai Chenhua Insrument Co., Ltd., China) were used in the experiment.

Multimode optical fibers with core diameter Φ 125 μm were purchased from Quanzhou Anpon Company, China. Au fibers with a diameter of 30 μm were obtained from Beijing Doublink Solders Co., Ltd, China. β-D(+)-glucose, GOD (activity 50 U mg^{-1}, Sigma), acetone, absolute ethyl alcohol (AR, Tianjin Kemiou Chemical Reagent Co., Ltd), sodium hydrate, zinc acetate dihydrate, zinc nitrate and hexamethylenetetramine (NaOH, $Zn(CH_3COO)_2 \cdot 2H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $C_6H_{12}N_6$, Tianjin Fuchen Chemical Reagent Factory) were used as the reagents in the experiment. Phosphate buffered solution (PBS, pH 7.4) was prepared with certain amount of $Na_2HPO_4 \cdot 12H_2O$ and KH_2PO_4 in de-ionized water. All other chemicals were of analytical grade.

2.2 Fabrication of spirally hierarchical structure-based working electrodes

A spirally hierarchical structure-based glucose sensor contained a working electrode, an Ag/AgCl reference electrode and a Pt auxiliary electrode, and the fabrication of the working electrode includes the construction of a microscale Au cylindrical spiral and the synthesis of ZnO nanowires. A multimode optical fiber was immersed in acetone for 5 min, and then the optical fiber core was pulled out from its sheath. One end of the Au fiber was fixed with epoxy resin on one end face of the optical fiber core, then manually the Au fiber was cylindrically spiraled around the optical fiber core, and eventually an Au cylindrical spiral with axial length 3 mm was formed. The other end of the Au cylindrical spiral was fixed with epoxy resin on the optical fiber core, and was also regarded as the lead of the working electrode. The assembly was cleaned in absolute ethyl alcohol in the ultrasonic washer and dried in the vacuum drier.

The synthesizing parameters of the hydrothermal method for ZnO nanowires included Zn^{2+}concentration of the seed layer solution and the growth solution, the growth time and the growth temperature. Six Au cylindrical spirals were immersed into the seed layer solution with 1 mM Zn^{2+} for 1 min, then annealed in 150 ºC for 10 min. The aforementioned immersing and annealing processes were repeated twice. Six Au cylindrical spirals with ZnO seed layer deposited on were put into the growth solution with Zn^{2+} concentrations of 0, 25, 50, 75, 100 and 125 mM respectively at 90 ºC for 2.5 h, then taken out, cleaned with de-ionized water for 5 min in the ultrasonic washer, and dried at room temperature. By these steps, 6 spirally hierarchical structures with different surface morphologies were obtained, and the results were shown in Fig.1. The spirally hierarchical structures above were immersed into 40 mg mL^{-1} GOD solution for 30 min, then taken out and dried at room temperature. Therefore GOD was immobilized on the surfaces of the spirally hierarchical structures. The samples were cleaned with de-ionized water to remove extra GOD, and dried at room temperature, and eventually 6 spirally hierarchical structure-based working electrodes were obtained.

2.3 Characterization of spirally hierarchical structures and corresponding working electrodes

Based on the micrographs of SEM and filtration, line edge detection and fitting operators of MATLAB software, the profiles of the spirally hierarchical structures without and with GOD were extracted, and further the geometric parameters such as the actual pitch, the actual helix angle and the actual outer diameter as well as the characteristic parameter of the surface morphologies were determined.

Among the characteristic parameters of a random rough surface, root-mean-square roughness (Ra) is defined as the 2nd moment of a random variable and describes the surface height fluctuation relative to the median surface. Skewness (Sk) is the 3rd moment of a random variable and suggests the symmetry of peaks and valleys relative to a Gaussian distribution. Kurtosis (Ku) is the 4th moment of a random variable and describes the fluctuation range of the surface heights compared with a Gaussian distribution. Correlation length (ξ) describes the distance between every two neighboring correlated surface heights.

2.4 Electrochemical characterization of spirally hierarchical structure-based glucose sensors