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Enzymatic glucose sensor based on Au nanoparticle and plant-like ZnO film modified electrode

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ABSTRACT

A novel electrochemical glucose sensor was developed by employing a composite film of plant-like Zinc oxide (ZnO) and chitosan stabilized spherical gold nanoparticles (AuNPs) on which Glucose oxidaze (GOx) was immobilized. The ZnO was deposited on an indium tin oxide (ITO) coated glass and the AuNPs of average diameter of 23 nm were loaded on ZnO as the second layer. The prepared ITO/ZnO/AuNPs/GOx bioelectrode exhibited a low value of Michaelis–Menten constant of 1.70 mM indicating a good bio-matrix for GOx. The studies of electrochemical properties of the electrode using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) showed that, the presence of AuNPs provides significant enhancement of the electron transfer rate during redox reactions. The linear sweep voltammetry (LSV) shows that the ITO/ZnO/AuNPs/GOx based sensor has a high sensitivity of 3.12 $\mu A \cdot mM^{-1} \cdot cm^{-2}$ in the range of 50 mg/dL to 400 mg/dL glucose concentration. The results show promising application of the gold nanoparticle modified plant-like ZnO composite bioelectrode for electrochemical sensing of glucose.

1. Introduction

Glucose sensing devices find important applications in clinical diagnostics and food industry. It was in 1962 when the initial enzyme-based electrochemical sensor for glucose detection was proposed by Clark and Lyons [1]. Afterwards tremendous efforts have been devoted to the fabrication of glucose sensors with high sensitivity, selectivity, stability and precise monitoring methods. While most of the commercial products are enzymatic glucose sensors due to their good selectivity, they are still facing challenges in sensing performance such as sensitivity, stability and accuracy [1,2]. At the same time, it is of much importance to invent more effective and continuous glucose monitoring techniques including invasive and non-invasive monitoring methods [1–3]. Lots of efforts are being made for the development of a stable bio-matrix for enzyme immobilization, and exploiting higher efficiency and productivity of the enzyme activity.

Electrochemical glucose sensors such as amperometric and potentiometric sensors are potential sensing techniques for continuous monitoring devices because of their high detection accuracy and wider sensing range [3,4]. By means of the advanced nanomaterial fabrication techniques, various micro- and nano-structure materials are being recently employed in the preparation of the electrodes for electrochemical glucose sensors. Materials such as metal oxides, conductive polymers, and nanocomposites are chosen as electrode materials to improve the biosensor activity by enhanced electron transfer rate, good biocompatibility, and excellent chemical stability [2,4]. A good candidate for biosensor matrix, micro- and nano-structured ZnO has attracted much attention due to its good chemical stability, biocompatibility, and tunability to achieve various different structures [5–9]. Most importantly, electrodes modified by a ZnO matrix provide a good bio-environment and affinity for enzymes, such as GOx. This is because enzymes like GOx are negatively charged and have low isoelectric points (IEP ~4.2) whereas ZnO provides a positively charged state in a neutral condition with a high IEP of around 9.5 thereby making very high affinity to each other. The presence of AuNPs has been shown to increase the amperometric signal significantly in enzymatic composite material bioelectrodes [10–14]. By attaching AuNPs to the enzyme, a bridge is created which connects the electron transfer from the electrode to the inner-shell active center of the enzyme, thus further assisting the direct electron transfer in the process of glucose oxidation.

In the present study, we report on the fabrication of a novel electrode for electrochemical glucose sensor by modifying plant-like ZnO nanostructures with AuNPs. The prepared composite working electrode, ITO/ZnO/AuNPs/GOx, showed excellent glucose sensing properties. The performance of the bio-electrode was thoroughly evaluated using EIS, CV and LSV measurements.

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2. Experimental

2.1. Chemicals and apparatus

Glucose oxidase (*Aspergillus niger*, type VII, lyophilized powder), D-(+)-glucose (99.5%), chitosan (low molecular weight, ~50,000 g/mol, 85% deacetylated), zinc oxide powder (99.99%, metals basis), and ITO glass slides (8–12 Ω/sq) were purchased from Sigma Aldrich. Hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9%), glacial acetic acid, potassium hexacyanoferrate (III) ($K_3[Fe(CN)_6]$), potassium hexacyanoferrate(II) trihydrate ($K_4[Fe(CN)_6] \cdot 3H_2O$, 98 + %), zinc oxide (99.99%), Nafion (D-520 dispersion, 5% w/w in water and 1-propanol), and phosphate-buffered saline (PBS, 10×, pH 7.4) were purchased from Alfa Aesar. The PBS was diluted to 1× for use. All other reagents were used as received without further purification. Deionized (DI) water was used in the preparation of electrolyte solutions.

The EIS, CV, and LSV studies were carried out using a potentiostat/galvanostat/ZRA using a three-electrode cell configuration with saturated silver chloride electrode (SCE) as a reference electrode and platinum foil as a counter electrode. The electrolyte was prepared in PBS, containing 5 mM $[Fe(CN)_6]^{3-/4-}$. The EIS, CV, and LSV were performed in 15 mL of the electrolyte solution. All glucose stock solutions were stored at 4 °C after preparation.

The structural and morphological characterization of the prepared ZnO was performed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD experiments were carried out using a Philips X'PERT X-ray diffractometer with 2θ varying from 20° to 80° and a step size of 0.02°/s. The analysis of diffraction patterns was carried out using the Rietveld technique. SEM images were collected on an FEI Quanta 600F scanning electron microscope at an accelerating voltage of 7 kV. The TEM images of AuNPs were taken using an FEI Tecnai TF20, 200 keV transmission electron microscope. For TEM, the sample was prepared by placing a drop of the colloidal solution on a Formvar/carbon-coated copper grid and allowing the solvent to evaporate at room temperature.

2.2. Preparation of plant-like ZnO and Au nanoparticles

The plant-like ZnO was prepared by a low-temperature solution based method by a modified procedure reported earlier [15]. Typically, 0.5 g of ZnO powder was dissolved in 20 mL of concentrated nitrate acid and then the solution was diluted using a suitable amount of DI water so that the concentration of ZnO becomes 0.005 M. A portion of this solution (50 mL) was taken and the pH was adjusted to 7 by adding 30 wt.% ammonia solution followed by heating at 50 °C for 30 min under constant stirring and then cooled down to room temperature

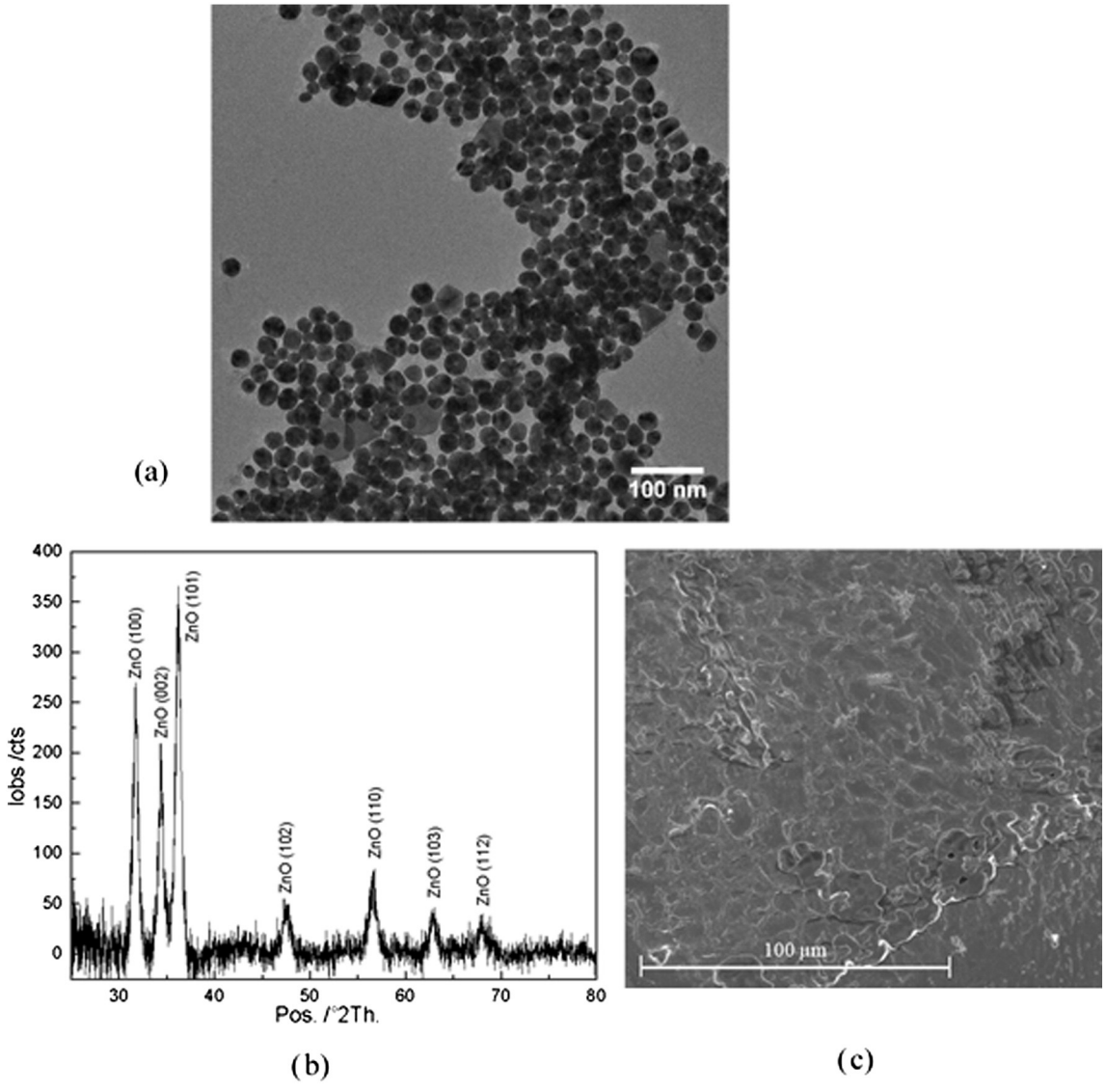

Fig. 1. (a) TEM images of gold nanoparticles; (b) XRD pattern of ZnO film prepared by solution based method; (c) SEM image of ZnO film on ITO glass.