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Effect of platinum-nanodendrite modification on the glucose-sensing properties of a zinc-oxide-nanorod electrode

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ABSTRACT

The properties of ZnO nanorods (ZnONRs) decorated with platinum nanodendrites (PtNDs) were studied. Various sizes of PtNDs were synthesized and spin coated onto ZnONRs, which were grown on indium–titanium–oxide (ITO) substrates through a low-temperature hydrothermal method. Scanning electron microscopy and X-ray diffraction analyses were conducted to analyze the morphology and structural properties of the electrodes. The effects of PtND size, glucose concentration, and Nafion amount on glucose-sensing properties were investigated. The glucose-sensing properties of electrodes with immobilized glucose oxidase (GO_x) were measured using cyclic voltammetry. The bio-electrochemical properties of Nafion/GO_x/42 nm PtNDs/ZnONRs/ITO glucose sensor was observed with linear range within 1–18 mM, with a sensitivity value of 5.85 μA/mM and a limit of detection of 1.56 mM. The results of this study indicate that PtNDs/ZnONRs/ITO has potential in glucose sensor applications.

1. Introduction

Diabetes mellitus is one of the leading causes of death and disability worldwide. This ailment is also highly responsible for heart disease, kidney failure, and blindness. The human body regulates blood glucose levels at a concentration of 4–8 mM (70–120 mg dL^{-1}). Diabetic patients exhibit a persistently high glucose level because they are unable to regulate their sugar level [1]. Glucose biosensors, which are used to monitor blood glucose level, are the most widely studied sensor. The most common application of nanotechnology for sensors in diabetes detection involves nanomaterials to support the standard enzymatic electrochemical detection of glucose. Incorporating nanoparticles into these sensors results in increased surface area, more efficient electron transfer from enzymes to electrodes, and enhanced ability to include additional catalytic steps. Different metal nanoparticles, such as Au, Pt, Ag, Fe, Zn, Cu, Pd, and Ir, are incorporated into the electrode surface of glucose sensor as modifiers, labeling factors, or immobilizer agents [2,3]. Metallic Au or Pt nanoparticles (PtNPs) have been embedded in a glucose sensor device. Au has higher work function at 5.1 eV, and it is more chemically stable compared with other nanoparticles. However, Pt also exhibits better sweep current and higher work function (5.65 eV) than Au (5.1 eV). Thus, PtNPs should show better retention and chemical stability [4]. PtNPs also exhibit good analytical performance with high sensitivity in a 1.0×10^{-4} to 0.1 mM range of linearity and 0.20 μM detection limit for the prepared glucose sensor [5]. PtNPs are expected to enhance and improve the performance of glucose sensor because these materials possess excellent electrical properties and higher work function than other nanoparticles [4].

The shape of PtNPs should be considered when PtNPs are used as a glucose sensor. Nanoparticles of different shapes tend to behave differently. Among the nanoparticles, PtNPs with a dendritic structure have received particular interest because they can provide a relatively large specific surface area and a high specific activity because of the presence of a large number of edges, sharp tips, and corners on their branches [6]. The sharp tips in platinum nanodendrites (PtNDs) have great tendency to enhance electric field and produce strong local enhancement of electromagnetic field [7].

The use of nanomaterials to assist the standard enzymatic electrochemical detection of glucose is the most common application of nanotechnology for diabetes sensors. Metallic nanoparticles, such as PtNDs-based electrode, show good catalytic activity toward many compounds, particularly glucose and H_2O_2. Electrodes modified with PtNDs through chemical reduction are employed for electrocatalytic glucose biosensing with enzyme in phosphate buffer solution (PBS). This type of glucose sensor achieves a linear

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range of 1–20 mM with a detection limit of 1.2 mM and a sensitivity of 12.1 mA mM^{-1} cm^{-2} [8]. However, PtND-based electrode exhibits several fatal drawbacks that prevent its direct application in enzymatic biosensors. Many species may adversely affect the physiological conditions of the PtND surface, particularly chloride anions that are strongly absorbed on the Pt surface; this phenomenon renders the electrode surface inaccessible to analytes [9]. PtND-based electrode in glucose sensor shows fatal drawbacks, such as the chemisorption of many organic species in the blood, including amino acids, ascorbic acid, uric acid, creatinine, and epinephrine, which severely reduce the electrocatalytic activity of Pt electrode when the electrode is used [10]. Moreover, the small current responses of target molecules caused by the slow reaction and electron transfer kinetics, which cannot compete with the interferential current from the electroactive species, result in the poor selectivity of PtND electrode as a biosensor. Thus, nanotechnology has opened new and interesting opportunities for exploring glucose biosensing applications of newly prepared nanostructured metal oxides to overcome the limitations of metal nanoparticles.

ZnO as nanostructured metal oxide has been extensively studied for its application in biosensors with high sensitivity, fast response time, and stability in determining glucose by electrochemical oxidation. Among the many nanostructured ZnO compounds, ZnO nanorods (ZnONRs) are widely analyzed for biomolecule immobilization. ZnONRs possess high surface area to volume ratio, reproducible sensitivity in short response time, and low detection limit. This nanostructure can easily act as an enhancing agent that effectively accelerates the electron transfer between electrode and detection molecules, thus resulting in rapid current response for target molecules. The nanostructured ZnO exhibits high sensitivity but extremely poor stability because the ZnO nanostructure is easily removed from the electrode surface during functionalization [11]. The high surface area to volume ratio of ZnONRs improves the immobilization of glucose oxidase (GO_x) that results in better electrical contact to the electrode [12]. Umar et al. [13] used ZnONRs for enzyme immobilization. The prepared glucose sensor shows high and reproducible sensitivity of 23.7 μA/cm^2 mM, detection limit of 0.37 nA, and linear dynamic range from 1 nA to 500 nA. Although the nanostructured ZnO exhibits high sensitivity, it showed extremely poor stability because the ZnO nanostructure is easily removed from the electrode surface during functionalization. Thus, improving the stability of the ZnO nanostructure without reducing sensitivity or selectivity is a significant challenge in glucose monitoring.

Extensive efforts have been expended to overcome these drawbacks by modifying the electrode substrate with metal and metal-based oxide nanomaterials to produce nanocomposites because the key factor that affects both the sensitivity and selectivity of glucose detection is the electrocatalytic activity of the immobilized GO_x [14]. Research interest in metal/metal oxide nanocomposites for enzymatic glucose sensing has recently increased. ZnO/PtNP heterostructures conjugated with GO_x exhibit good analytical performances with high sensitivity of 62.14 μA/cm^2 mM in a wide linear range, and low detection compared with bare ZnO/GO_x biosensors with 30.16 μA/cm^2 mM [15]. However, fabrication and performance of PtNDs on ZnONR electrodes as glucose sensor have not been reported. Thus, in this work, the sensitivity and response problems of bare PtND and ZnONR electrode enzymatic glucose-sensing could be alleviated by utilizing nanocomposite materials, such as PtNDs/ZnONRs. Compared with bare ZnONR and PtND electrodes, PtNDs/ZnONRs demonstrated excellent electronic conductivity and good biocompatibility, as well as enhanced the electron transfer between glucose and the electrode surface [16]. PtNDs/ZnONRs also showed that prepared glucose sensor exhibits high sensitivity and good operational stability for glucose detection.

Several methods incorporated Pt to ZnO matrices to produce PtNDs/ZnONRs nanocomposite materials by self-assembly and electrodeposition, among others. However, no works on the formation of PtNDs/ZnONRs by the spin-coating method have been reported. In this work, spin coating was adopted to form PtNDs/ZnONRs/indium–titanium–oxide (ITO). The spin-coating process uses centrifugal forces to distribute liquid radial outward. Compared with other thin film deposition techniques, spin coating is fast, convenient, and reproducible method that results in uniform film thickness on a substrate [17].

In this work, various sizes of PtNDs were synthesized by changing the precursor K_2PtCl_4 concentrations via chemical reduction. The morphological, structural, and glucose-sensing behavior of PtNDs was studied based on PtND size, glucose concentration in 0.01 M PBS, and Nafion amount added to the nanocomposite. The observed properties were systematically discussed.

2. Experimental details

ZnONRs were grown on ITO substrates. The ITO glass substrates were cleaned using a Radio Corporation of America cleaning (Type II) that consists of a mixture solution of water (H_2O), ammonium hydroxide (NH_4OH), and hydrogen peroxide (H_2O_2) in a volume ratio of 20:4:1. The mixture solution in the beaker was heated on a hot plate to 60 °C. The temperature was constantly controlled and maintained at 60 °C for 20 min. After 20 min of heating, ITO glass substrates were cleaned three times with deionized (DI) water. For further cleaning, the ITO glass substrates were also immersed in propanol about 2 min and dried. ZnO seed layers were prepared by dissolving zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) in methanol. The mixture was vigorously stirred at 60 °C for 20 min. Monoethanolamine was added dropwise into the solution under constant stirring at 60 °C for 2 h. The solution was aged at room temperature for 24 h before the deposition process. A total of 20 μl of ZnO seeds was dropped on the ITO substrates (1 cm^2) and dried in an oven at 150 °C. This process was repeated three times. Afterward, the coated ITO substrates were annealed in the furnace at 500 °C for 2 h in air. The ZnO seeded samples were placed in the screw-capped bottles containing a 1:1 molar ratio of zinc nitrate tetrahydrate ($Zn(NO_3)_2{\cdot}4H_2O$) and hexamethylenetetramine and $C_6H_{12}N_4$ as the precursor solution [18]. The hydrothermal reaction was performed in a preheated oven at 80 °C for 4 h. Subsequently, the samples were removed from the screw-capped bottle and cleaned using DI water several times. All the samples were dried in an oven at 90 °C for 1 h.

PtNDs were synthesized through chemical reduction. Various concentrations of K_2PtCl_4 solution were prepared in water to produce different sizes of PtNDs: 5, 10, 15, 20, and 25 mM. Pluronic F127 (20 mg) was then added to the prepared K_2PtCl_4. Next, 2 ml of 88% formic acid was rapidly added to the solution and maintained under constant stirring to ensure that all chemicals were dissolved and mixed well. The mixed solution was immersed in an ultrasonic bath for 12 min. After the reaction completed, the PtND suspension was washed three times with DI water. The residue was removed through centrifugation at 9000 rpm for 20 min. Afterward, 4 ml of DI water was added to each sample, and the colloidal sample of PtNDs was stored at room temperature.

To prepare PtNDs enhanced with ZnONRs, 20 μl of different PtND sizes were spin coated on top of the prepared ZnONRs/ITO at 5000 rpm for 50 s. The process was repeated three times. The samples were cured in an oven at 160 °C for 1 h to evaporate the organic impurities and achieve good adhesion with the substrate.

To fabricate the glucose sensor, GO_x enzyme solution was freshly prepared by dissolving 1 mg of GO_x in 1 ml of 0.01 M PBS to immobilize GO_x enzyme over PtND/ZnONR-modified