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Synthetic Metals

Non-enzymatic glucose sensor based on copper oxide and multi-wall carbon nanotubes using PEDOT:PSS matrix

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ABSTRACT

A non-enzymatic glucose sensor based on a pencil graphite electrode (PGE), a modifier suspension including the conducting polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and CuO nanoparticles was developed. Then it was subjected to cyclic voltammetry and chronoamperometry to evaluate the electrochemical performance of the modified electrode. This sensor showed good catalytic activity, sensitivity and wide linear range. In addition, the effect of addition of multi-wall carbon nanotubes (MWCNTs) to the modifier suspension on the activity of sensor towards glucose was investigated. The PEDOT:PSS/CuO/MWCNTs-PGE based sensor exhibited better electrocatalytic activity towards glucose. At an applied potential of $+0.70\,V$ (vs. Ag/AgCl), this sensor presented an acceptable sensitivity of $663.2\,\mu A\,mM^{-1}\,cm^{-2}$ in a wide linear range up to 10 mM. It, also, showed excellent reproducibility (relative standard deviation of 1.1% over seven identically fabricated electrodes), very good long-term stability (only 7% loss in current response over a period of one month), and excellent anti-interference ability in the existence of common interfering species.

1. Introduction

In-vivo and in-vitro glucose level determination in blood or other sources such as foods and pharmaceuticals is very important [1]. It is estimated that 400 million people are affected by diabetes [2]. Therefore, the need to diagnose and monitor this disease has caused much attention in recent years. This fact leads to the growing demand for the investigation and production of rapid, accurate and reliable glucose sensors.

In recent decades, enzymatic glucose biosensors have been commercially used to determine glucose levels in a great extent. However, there are disadvantages of using enzymes due to inherent flaws of enzymes including high production cost; complicated immobilization procedures; poor stability; and high sensitivity to pH, temperature and humidity. Therefore, attention has recently being paid to non-enzymatic glucose sensors which display features like low production cost, reproducibility, simplicity, high stability, and high sensitivity [3,4]. In non-enzymatic glucose sensors, glucose levels are determined through electrochemical oxidation of glucose using different electrocatalysts. Cobalt oxide, nickel oxide, copper oxide and zinc oxide are the most attractive electrocatalysts to sensor researchers due to their low cost, high transfer kinetics of electrons, chemical stability, high glucose adsorption, and satisfactory biocompatibility. Nevertheless, low electronic

conductivity and catalytic activity of metal oxides are two major barriers to commercialization. Thus, efforts have been made to employ conjugate metals or carbon materials, in particular, carbon nanotubes and graphene to overcome these problems [2,5–7]. Moreover, the use of nanostructured metal oxides can be the best choice in non-enzymatic glucose sensors since they increase active sites and improve interfacial contact between the metal oxides and glucose [2].

Conducting polymers (CPs) have been used as electrode coatings, to improve the physico-chemical properties of bare electrodes in various fields of chemical and biological sensors [8,9]. To improve the performance of glucose biosensors, a conducting polymer can be used as an efficient electron transfer medium and also as a stable matrix for the biocomponent immobilization. These polymers are employed as redox-mediators to act toward a variety of analytes, to increase sensitivity and/or selectivity, and to reduce detection limit. Polypyrrole (PPy), Polyaniline (PANI), and Polythiophene (PT) are conducting polymers which are mostly used in enzymatic biosensors [10–15]. In order to achieve better catalytic activity in non-enzymatic glucose sensors, the conducting polymer can act as a host to immobilize the metal nanoparticles. For this purpose, CPs such as PANI, PPy, PT, and poly(3,4-ethylenedioxythiophene) (PEDOT) have been used as a host matrix of nanoparticles [16–18]. Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) has been successfully used as gas

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sensors [19,20] and biosensors [21,22] due to its excellent physical properties such as solubility in water, high conductivity, and good electrochemical and physical stability. This polymer has, also, been used to improve the performance of enzymatic glucose biosensors [15,23,24], but to our best knowledge, has not been applied to modify the properties of non-enzymatic glucose sensors using CuO.

Although pencil graphite electrode (PGE) has been successfully used in the cathodic and anodic voltammetry due to its high electrochemical reactivity, good mechanical rigidity, low cost, simple technology, and easy modification [25], in most of literature, PGEs were only used in enzymatic glucose biosensors [26,27]. It is worth mentioning that the voltammetric response of analyte is highly affected by the nature of the pencil lead type [28]. According to Kariuki et al. [29,30], HB graphite leads showed electron transfer rates similar to those of glassy carbon electrodes (GCEs) compared with other types of pencil graphite. HB leads also generated a high analyte signal and relatively low noise. Additionally, the strict quality control of the pencil leads during the manufacturing process, results in a uniform composition and surface finish. Similar analytes' voltammetric signals recorded on PGEs of the same type indicate good electrode-to-electrode reproducibility [28]. One concern in regards to the use of commercial pencil leads as the working electrode is the difference in electrochemical behaviour of pencil leads produced by different manufacturers. According to Tavares and Barbeira [31], graphite pencil leads of the same hardness but produced by various manufacturers exhibit the same voltammetric behaviour although the graphite pencil leads produced by Faber-Castell and Pentel showed higher reproducibility compared with pencil leads produced by Kappel. Therefore, in this work, a Faber-Castell HB pencil lead was used as the working electrode; then a suspension was prepared to modify the electrode. This modifier suspension composed of PEDOT:PSS and multi-wall carbon nanotubes (MWCNTs); both used to improve electron transfer. CuO nanoparticles were dispersed into the suspension to function as the direct oxidant of glucose. A drop-coating technique is employed for the modification of pencil graphite electrodes which is an inexpensive and up-scalable method. The modified PGEs then were subjected to electrochemical measurements to evaluate their activity and reliability towards glucose sensing. The experimental outcomes were compared with other CuO based non-enzymatic glucose sensors in terms of the main analytical characteristics including operational potential, sensitivity, linear range, and detection limit.

2. Experimental

2.1. Chemicals

D-(+)-Glucose was purchased from BDH. CuO nano powder with a purity of 99.9% and average particle size of 40–80 nm was acquired from Advanced Materials. Multi-wall carbon nanotubes (MWCNTs) with 60–80 nm in outer diameter and 10–15 μm of average length prepared by chemical vapour deposition, were purchased from Shenzhen Nanotech Port Ltd. Co. (China). An aqueous dispersion of PEDOT:PSS (1.3 wt% solid content), ascorbic acid, uric acid, dopamine, fructose, lactose, and sucrose were purchased from Sigma-Aldrich. 72,000 g mol^{-1} polyvinyl alcohol (PVA) was obtained from Merck. Also, 0.1 M sodium hydroxide solution (NaOH) was used as the supporting electrolyte. All chemical reagents were of analytical grade. All solutions were prepared using deionized water.

2.2. Construction of pencil graphite electrode

Fig. 1 shows the schematic of PGE used as working electrode, modification processes, and the final modified electrode. For the construction of PGEs, Faber-Castell HB hardness graphite pencil leads with a 2 mm diameter were employed. The graphite leads, initially 130 mm long, were cut in 20 mm. An electrical contact was made by soldering a high-conductivity copper wire to the pencil lead. Then, the graphite

lead and solder were placed in a glass tube and a fast-drying epoxy resin (~2 min) was used to seal and attach the electrodes to the glass tube. After the epoxy resin dried, the glass tube was broken and the electrode was carefully polished with 0.3 μm alumina suspension. Then, the electrodes were cleaned with ultrasonic cleaning bath and water; their surfaces, then, were washed with ethanol.

2.3. Pencil graphite electrode modification

To clean multi-wall carbon nanotubes (MWCNTs), first 0.1 g MWCNTs were suspended in 50 mL of concentrated HNO3. This suspension then ultrasonicated for 2 h followed by stirring for 12 h. The powder was collected on a filter paper and then washed for several times with distilled water until reaching to the neutral pH. Finally, MWCNTs were dried at 90 °C overnight. Through a suitable combination of stirring and sonication and without any stabilizer or dispersant, CuO nanoparticles can be stabilized in water for a long time [32,33]. Hence, in this work, an aqueous-based conducting polymer was used as the base for CuO nanoparticles. To provide a suspension by which the PGEs are modified and prepared for the electrochemical experiments, 0.5 wt% CuO nanoparticles was added to the matrix of PEDOT:PSS conducting polymer. To investigate the effect of MWCNTs on the electrochemical performance of the sensor, another modifier suspension containing PEDOT:PSS, 0.5 wt% CuO nanoparticles, and 0.2 wt% MWCNTS was prepared. After adding these nanoparticles to the PEDOT:PSS, both modifier suspensions were stirred for 12 h and then sonicated for 90 min by a probe sonicator. Also, to increase the adhesion of the polymeric layer to the PGE surface, 5 wt% PVA was used as a coating layer on the PEDOT:PSS polymer surface. To prepare 5 wt% PVA solution, 1 g PVA was added to 20 ml of water and stirred for 2 h at 70 °C using a magnetic stirrer.

To apply the modifier suspensions on the electrodes surface, a very easy and inexpensive technique of drop-coating was used. First 5 μL of PEDOT:PSS/CuO suspension or PEDOT:PSS/CuO/MWCNTs suspension was dropped onto the reaction area of the PGE and then air-dried. After drying, the same method was employed to apply a PVA layer on the electrode reaction area. These electrodes can be re-used provided that their surfaces are thoroughly water-washed in an ultrasonic cleaning bath and are subsequently alcohol-washed.

2.4. Electrochemical measurements

To evaluate the electrochemical performance of the sensors, cyclic voltammetry (CV), and chronoamperometry (CA) measurements were performed using Potentiostat/Galvanostat Autolab30 (from EcoChemie, NL) with General-Purpose Electrochemical System software package (GPES 4.9) in a conventional three-electrode cell. This cell includes a modified PGE as the working electrode as well as an Ag/AgCl electrode and a Pt electrode as the reference electrode and the counter electrode, respectively. Electrochemical measurements were conducted at room temperature and a freshly prepared electrolyte solution was used for each measurement. To investigate the activity of modified electrodes towards glucose oxidation, CV measurements were carried out in the presence and absence of 4.0 mM glucose in 0.1 M NaOH solution at a scan rate of 50 mV s^{-1}. Since the catalytic reactions of glucose involve the presence of OH$^-$ group, the effect of pH on the electrochemical behaviour of the PEDOT:PSS/CuO modified PGE was studied using cyclic voltammetry in four various concentrations of NaOH solutions. CA measurements for different glucose concentrations were performed at a working potential of +0.70 V (vs. Ag/AgCl) without stirring. To avoid the degradation and fatigue phenomenon due to repetitive measurements using the same electrode [34], a new modified electrode was utilised for the investigation of current response to each glucose concentration. The calibration curve was plotted using the data obtained from CA measurements after 20 s for different glucose concentrations. The sensitivity was also calculated from the slope of