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Electrochemical and nonenzymatic glucose biosensor based on MDPA/MWNT/PGE nanocomposite

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ABSTRACT

The nonenzymatic detection of glucose has been widely investigated in a variety of fields ranging from biomedical applications to ecological approaches. Among these fields, electrochemical methods have great advantages such as high electrocatalytic ability, high sensitivity, good selectivity and low-cost for the electrooxidation of glucose. Future trends on glucose sensing are nanostructured electrodes depending upon the development of nanotechnology. In this study, an electrochemical and nonenzymatic glucose sensor based on (*E*)-4-((5-methylthiazole-2-yl)diazenyl)-*N*-phenylaniline (MDPA)/multi-walled carbon nanotube (MWNT)/pencil graphite electrode (PGE) was performed. Electrochemical measurements were obtained using cyclic voltammetry and square wave voltammetry techniques, and characterization of surfaces was carried out using scanning electron microscope and electrochemical impedance spectroscopy techniques. The modification of PGE was made using MDPA and MWNT, and 10 cycles coating was used to prepare the proposed electrode. The effects of scan rate and pH on the peak potential and the peak current were determined. The limit of detection and linear range were calculated using various concentrations of glucose. The interference study was made using coexisting substances including metal ions such as Al^{3+}, Cu^{2+}, Fe^{3+} and ascorbic acid.

1. Introduction

Carbon nanotubes (CNTs) consist entirely of carbon and belong to a family of nanomaterials. In this family, multi-walled carbon nanotubes (MWNTs) are multiple layers of superimposed graphite and form a tubular shape rolling on themselves. These cylindrical graphite structures are polymers of pure carbon and can be reacted using the rich chemistry of carbon. This advantage provides opportunity to modify various surfaces allowing innovative applications in optics, electronics, materials, chemical processing and electrochemistry [1]. The structure of MWNTs was represented in Fig. 1, inset (a).

Organic dyes, especially azo dyes can combine with MWNTs with strong π-π interactions to form stable hybrids [2]. Various applications of MWNTs with azo dyes have been already reported [3–5]. Electrocatalytic activity of these combinations gains great advantages such as high mechanical stability and sensitivity for different electrochemical techniques possessing excellent responses to various substances such as redox proteins [6], drugs [7], small biomolecules [8], hormones [9], and so on. (*E*)-4-((5-methylthiazole-2-yl)diazenyl)-*N*-phenylaniline (MDPA) is a novel azo dye that can be synthesized by a coupling reaction in two stages: dinitration and coupling. Therefore, MDPA was selected as a new modification mediator in line with MWNT. The structure of MDPA (molecular weight, MW = 294.09 g mol^{-1}) was represented in Fig. 1, inset (b).

A number of studies have been used to monitor glucose levels in blood [10–12]. Among these studies, electrochemical and optical methods have been developed extensively. Glucose oxidase based electrochemical biosensors are widely preferred with the ability of high selectivity. However, these techniques can be affected by enzyme immobilization, pH and temperature [13]. Therefore, enzyme-free techniques are necessary on the direct electrochemical oxidation of glucose. The electrochemical and nonenzymatic detection of glucose is a cost-effective, rapid, sensitive and stable approach. In recent years, noble metals and alloys are used to fabricate nonenzymatic glucose sensors, but their applications are limited because of high cost [14]. Also, a large scale of platinum-based materials are commercially applied as nonenzymatic glucose sensors. However, their use is restricted by poor stability and high cost [15]. Therefore, various nanomaterials have been developed as excellent nanocatalysts to provide new surfaces on the fabrication of novel nonenzymatic glucose sensors. Among these materials, CNTs show unique physical and chemical properties, so they are widely used to fabricate enzyme-free glucose sensors. The first study was reported by Ye et al. using CNT modified electrode [16] and since then, researchers continue to develop novel CNT composites as nonenzymatic glucose sensors.

In this work, the strong noncovalent adsorption by π-π interactions of novel synthesized MDPA on the surface of MWNT/PGE was performed electrochemically, and the prepared stable, uniform and

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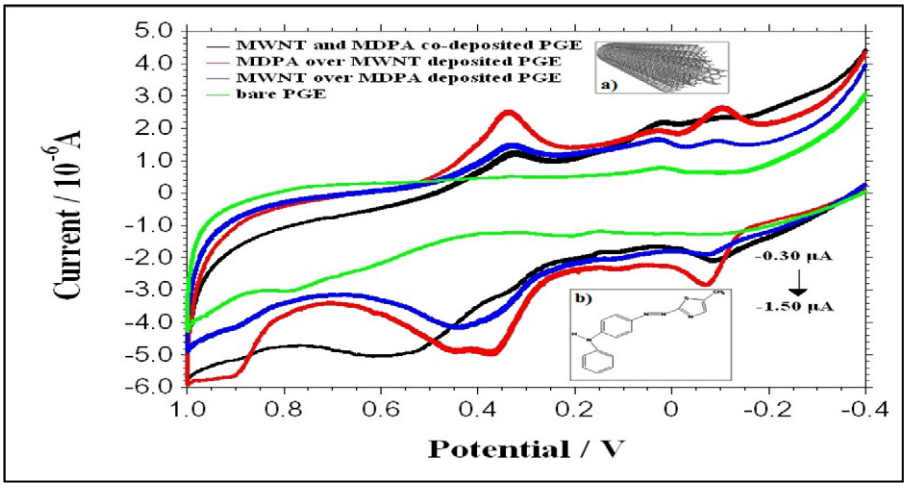

Fig. 1. Cyclic voltammograms of 1.0 mg mL^{-1} MWNT and 1.0 mM MDPA co-deposited PGE, 1.0 mM MDPA over 1.0 mg mL^{-1} MWNT deposited PGE, 1.0 mg mL^{-1} MWNT over 1.0 mM MDPA deposited PGE and bare PGE in BR buffer at pH 3.0 between −0.4 V and +1.0 V vs. Ag/AgCl. Inset: a) the structure of MWNTs and b) the structure of MDPA.

sensitive film (MDPA/MWNT/PGE) was used for direct determination of glucose for the first time. The improvement of electrooxidation response of glucose was completed using MDPA/MWNT/PGE nanocomposite. The surfaces of modified electrodes were characterized using scanning electron microscope and electrochemical impedance spectroscopy techniques. The effects of scan rate and pH on the peak potential and the peak current of glucose signal were determined. Interference studies were made to determine the selectivity of MDPA/MWNT/PGE for glucose.

2. Material and methods

2.1. Chemicals

COOH functionalized MWNTs from Nanografi (>95%, OD: 20–30 nm) were dissolved in water and the concentration of solution was adjusted to 1.00 mg mL^{-1}. MDPA was prepared as 1.00 mM in water. D-(+)-glucose (minimum 99.50%) from Sigma was dissolved in 0.10 M NaOH from Merck and the concentration was adjusted to 5.00 mM. Boric acid, phosphoric acid and acetic acid from Merck were used to prepare 0.20 M Britton-Robinson (BR) buffer solution and pH was adjusted to 3.00 by using 1.00 M HCl and 1.00 M NaOH from Merck. 0.10 M phosphate buffer solution (PBS) at pH 7.00 was prepared from pellet dissolving in 100.00 mL water. $K_4Fe(CN)_6$ from AnalaR Analytical Reagents, $K_3Fe(CN)_6$ from the Fischer Scientific Company and KCl from Merck were used to prepare a 0.10 M redox solution for electrochemical impedance spectroscopy. Metal ions containing $CuCl_2.2H_2O$, $Fe(NO_3)_3$ and $AlCl_3.6H_2O$ from Merck were used 275-folds concentrated as 0.25 g mL^{-1}. L (+)-ascorbic acid from Merck was used 132-folds concentrated as 0.12 g mL^{-1}. Other reagents were in analytical grade. In all analysis, pure N_2 gas was passed from all solutions for sufficient period of time to remove oxygen.

2.2. Instruments

Electrochemical experiments were performed on *CH Instruments CHI660C* model potentiostat with a conventional three electrode system which consisted of pencil graphite working electrode (PGE), silver/silver chloride reference electrode (Ag/AgCl) and platinum counter electrode. PGE was prepared using mechanical pencil *Model T 0.50* (Rotring, Germany) as a holder for pencil lead (Tombo, Japan) which was purchased from a local bookstore and a metallic wire was wrapped around the metallic part of the pencil to provide electrical contact to the lead. All leads had a total length of 60.00 mm and a diameter of 0.50 mm. A total of 10.00 mm of lead was immersed in solution per measurement. Surface area of PGE in such a length was 15.90 mm^2. SEM images of the modified surfaces were obtained using a *Zeiss Evo 60 EP-SEM* scanning electron microscope.

2.3. Deposition and surface morphologies of PGE

PGE surfaces were modified in 1.0 mM MDPA and 1.0 mg mL^{-1} MWNT solutions using 10 cycles coating by cyclic voltammetry (CV) between −1.0 V and +1.0 V vs. Ag/AgCl. The order of depositions was determined comparing the current enhancements of co-deposited, MDPA deposited and MWNT deposited PGEs in PBS at pH 7.0. The surface morphologies of PGEs were compared using scanning electron microscope (SEM) and electrochemical impedance spectroscopy (EIS) techniques. The superiority of MDPA over MWNT was accepted and the surface was titled as MDPA/MWNT/PGE.

2.4. Detection of glucose

The detection of glucose in 5.0 mM glucose/0.1 M NaOH solution was performed using square wave voltammetry (SWV) between −0.8 V and 0.0 V vs. Ag/AgCl. The detection limit and linear range of glucose were calculated and the effects of co-existing substances including metal ions and ascorbic acid were determined.

3. Results and discussion

3.1. The amount of deposition thickness

The coverage of deposition is an important parameter for electrochemistry because it can influence the surface area and possible interactions between substances [17–19]. High accumulation with increase number of cycle can decrease the current enhancement. Therefore, the optimum thickness for co-deposition and single depositions of MDPA and MWNT was determined using various number of cycles (5–20) between −1.0 V and +1.0 V vs. Ag/AgCl, and the current responses were compared in PBS at pH 7.0. As could be seen from Table 1, maximum current enhancements were obtained using 10 cycles (red colored) in all surfaces and the experiments were performed in this condition.

3.2. The order of deposition

The order of deposition of the carbon nanotubes and azo dyes, as well as their amounts of thickness, can influence the performance