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Original Article

Nonenzymatic glucose sensor based on disposable pencil graphite electrode modified by copper nanoparticles

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A B S T R A C T

A nonenzymatic glucose sensor based on a disposable pencil graphite electrode (PGE) modified by copper nanoparticles [Cu(NP)] was prepared for the first time. The prepared Cu(NP) exhibited an absorption peak centered at ~562 nm using UV-visible spectrophotometry and an almost homogenous spherical shape by scanning electron microscopy. Cyclic voltammetry of Cu(NP)-PGE showed an adsorption controlled charge transfer process up to 90.0 mVs^{-1}. The sensor was applied for the determination of glucose using an amperometry technique with a detection limit of [0.44 ($\pm$0.01) μM] and concentration sensitivity of [1467.5 ($\pm$1.3) μA/mMcm^{-2}]. The preparation of the Cu(NP)-PGE sensor was reproducible (relative standard deviation = 2.10%, n = 10), very simple, fast, and inexpensive, and the Cu(NP)-PGE is suitable to be used as a disposable glucose sensor.

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1. Introduction

The diagnosis and monitoring of diabetes was recently highlighted by a report in which it was stated that 20% of the total world population is affected by this chronic disease [1]. One of the proactive measures needed to control diabetes is the determination of blood glucose concentration with the aid of home-monitoring kits or reliable sensors. Therefore, the development of rapid, simple, and reliable methods of monitoring glucose is one of the most important human needs. As such, many studies have involved the use of enzymes such as glucose oxidase which provides great selectivity and sensitivity toward glucose determination. However, this strategy is limited by the poor stability, high cost of enzymes, complicated immobilization procedure, and critical operational conditions due to sensitivity of the enzyme to pH, temperature, humidity, ionic detergents, and toxic chemicals [2]. Therefore, a variety of approaches have been explored to develop nonenzymatic glucose sensors based on the direct oxidation of glucose for practical applications [3]. Because of their extraordinary physicochemical characteristics, nanomaterials such as noble metals [4], metal alloys [5,6], metal nanoparticles [7], metal nanoparticle decorated carbon nanotubes [8], and graphene [9] are of great interest for the fabrication of nonenzymatic sensors. However, most of these nonenzymatic sensors have displayed drawbacks such as the high cost of rare metal precursors, low sensitivity, narrow

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linear range, poor selectivity, and poisoning by adsorbed intermediates. Among the metals, copper attracts more attention due to its low cost, plenty of morphologies, high specific surface area, the possibility of promoting electron transfer reactions at lower overpotentials, and excellent electrocatalytic activity for glucose oxidation without poisoning [10]. It has been speculated that nonenzymatic electro-oxidation of glucose is greatly enhanced with copper compared with other metals as a result of its electrocatalytic effect mediated by Cu(II)/Cu(III) redox couples [11]. Copper electrodes are employed for the direct determination of carbohydrates in amperometric mode in strongly alkaline mediums without any electrode fouling [12,13]. In the past decade, a variety of copper nanomaterials including CuO [10,14], Cu(OH)$_2$ [15], and Cu(NP) incorporated into carbon nanotubes [15] and graphene [2] have been fabricated and applied for nonenzymatic determination of glucose.

Pencil graphite electrodes (PGE) have some advantages such as high electrochemical reactivity, commercial availability, good mechanical rigidity, disposable, low cost, low technology, and easy of modification. In addition, single-use disposable electrodes may overcome the regeneration drawback of the other solid electrodes. It was reported that PGEs offer a renewal surface which is simpler and faster than polishing procedures, common with solid electrodes [16]. In most reports PGEs were used for enzyme-based glucose determination [17]. For example, more recently PGEs have been used for immobilization of glucose oxidase for glucose biosensing [18,19]. A literature survey revealed that there are no studies to date on the use of copper nanoparticle-modified PGEs for nonenzymatic determination of glucose. Therefore, in the present study a PGE was modified by copper nanoparticles simply via a dip-coating method for the first time. The modified electrode was characterized by cyclic voltammetry and influenced parameters were optimized. The modified electrode was applied for high sensitive amperometric determination of glucose.

2. Methods

2.1. Reagents

Acrylic acid, ammonium persulfate, copper nitrate, hydrazine monohydrate, glucose, and other materials used were all analytical grade obtained from Sigma–Aldrich (Chemical Co, St. Louis, US). All solutions were prepared with double distilled water.

2.2. Synthesis of copper nanoparticles

Acrylic acid was added to 30 mL of distilled water and allowed to stir for 10 minutes. Ammonium persulfate initiator was then added to the reaction mixture and stirred until completion of polymerization and polyacrylic acid synthesis. In a typical synthesis of copper nanoparticles, a mixture of Cu(NO$_3$)$_2$ powder (18.7 mg) and polyacrylic acid (1 mL) were completely dissolved in water (20 mL) under sonication at 60°C for 20 minutes. Then, 0.5M NaOH (1 mL) was added dropwise to the solution to adjust the pH. After sonication for

20 minutes at 60°C, hydrazine (0.064 mL) was added to the sonicated solution. The reaction flask was kept in a water bath at 60°C for 30 minutes. The ruby red color of the solution indicated the formation of copper nanoparticles. This solution was added to the dialysis tube and dialysis was performed in distilled water for 24 hours to remove the excess of hydrazine and other impurities.

2.3. Modification of PGE with copper nanoparticles

PGE was pencil lead (Tombow Co., Ltd. Japan) with a diameter of 0.5 mm that was inserted into a Teflon tube exposing 0.5 cm of its tip (A = 0.15 cm^2). Electrical contact was made by soldering a metallic wire to the exposed reverse side of the PGE. To complete the modification, the bare PGE was immersed into the copper nanoparticles colloidal solution for about 60 minutes, then removed, and dried under an atmosphere of argon overnight.

2.4. Characterization

Electrochemical measurements were performed on Potentiostat/Galvanostat Autolab30 (from EcoChemie, NL) in a conventional three-electrode glass cell containing modified PGE as working electrode, a Pt rode as auxiliary electrode, and Ag/AgCl (3MKCl) as reference electrode. UV-visible (Vis) absorbance spectra were measured with a PG Instruments T90 Double Beam UV-Vis Spectrophotometer. Powder (PG Co., Ltd. UK) X-ray diffraction data were obtained with a D8-ADVANCE diffractometer (Bruker AXS, Karlsruhe, Germany) using CuKα radiation with a secondary graphite monochromator. The morphologies of the nanoparticles were investigated via scanning electron microscope (SEM; HITACHI 54160, Japan).

3. Results and discussion

3.1. Characterization of Cu(NP)

An image of the copper nanoparticles dispersion in distilled water is shown in Figure 1. UV-Vis spectrophotometry was carried out to confirm the formation of copper nanoparticles. A strong characteristic peak around 562 nm was noted for the copper nanoparticles due to the surface plasmon resonance effect [20]. The SEM image of the polyacrylic acid capped copper nanoparticles confirmed the prepared copper nanoparticles were almost homogenously spherical without exhibiting the irregular shapes and aggregation (Figure 1).

3.2. Characterization of Cu(NP)-PGE

Cu(NP)-PGE was prepared by dipping the PGE into the copper nanoparticles colloidal solution, then removing and drying the modified electrode. Cyclic voltammetry before and after modification was applied to monitor the whole process in preparation of Cu(NP)-PGE. Figure 2 shows the cyclic voltammograms obtained in 0.1M NaOH on the PGE (A) before and (B) after modification by copper nanoparticles. As expected there was no obvious redox peak in the cyclic voltammogram obtained on the bare PGE in the studied potential range. But on