Non-enzymatic Glucose Sensor Based on CuO Nanoplates

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Abstract

We have successfully fabricated an electrochemical sensor for non-enzymatic glucose measurement based on copper oxide (CuO) nanoplates. CuO nanoplates were synthesized by a facile hydrothermal method at 180 °C for 23 h without using any surfactants. Filed-emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD) were used to characterize morphologies and crystal structures of synthesized CuO nanoplates. A mixture of CuO nanoplates and polytetrafluoroethylene with mass ratio 0.15:1 was compressed at 9800 kPa onto platinum (Pt) to form Pt/CuO disk and it has been used as a working electrode for glucose measurement following non-enzymatic approach. Glucose concentration was evaluated by cyclic voltammetry in 0.1M NaOH solution. This enzyme-free electrochemical method was able to detect glucose with a concentration as low as 0.1 mM. These results show that CuO nanoplates are a promising candidate for non-enzymatic glucose detection.

Keywords: non-enzymatic glucose detection, CuO nanoplates, electrochemical method

1. Introduction

Diabetes mellitus is a type of metabolic disorders characterized by a high blood sugar level resulting from the dysfunction of insulin secretion. Long-term diabetes may cause multiple complications such as blindness, cardiovascular disorders, and kidney failure [1]. Therefore, it is a critical need to control and monitor the blood glucose level. For this reason, glucose sensors have been extensively researched and developed, especially for diabetes diagnosis [2].

Enzymatic glucose sensors have been extensively developed because of their broad applications in the food industry, biotechnology, clinical diagnostics, particularly in self-testing and continuous blood glucose monitoring [3]. The presence of glucose is detected by measuring the rate of glucose oxidation from the enzyme glucose oxidase. Electrochemical enzymatic glucose sensors have attracted great attention from researchers because of excellent selectivity and high reliability [2]. However, these sensors have some disadvantages such as naturally insufficient stability, loss of enzyme activity during the immobilization process [4], constraint on pH of 2-8, temperatures below 44°C, and ambient humidity levels [5]. Considering these disadvantages of the enzyme, non-enzymatic glucose sensors have attracted increasing research attention thank to their low cost, high stability, prompt

response, and low detection limit [2]. The fabrication of a wide variety of nanomaterials such as metals, metal oxides has introduced plenty of selective and highly responsive glucose sensors.

Among metal oxide materials, CuO nanostructures are widely studied materials and have been used to detect glucose [6] because of its electrochemical activity which promotes electron-transfer reactions even at a lower overpotential [7]. CuO nanostructures with different structures such as nanoparticles [8], nano bricks [7], nanoseeds [9][10], nanowires [11] have been used to measure glucose concentration with the limit of detection in the order of μmol/L. The modification of CuO nanostructures with other materials such as carbon nanotubes [12], graphene [13], ZnO nanorods [14] exhibits enhanced electrochemical properties and also enhanced glucose detection. However, the number of studies on the use of CuO nanostructures applied to the detection of biological objects is still limited. Furthermore, there are no studies related to the fabrication and use of CuO nanoplates for biosensor applications.

In this work, CuO nanoplates were prepared by a surfactant-free hydrothermal method. Then, CuO nanoplates have been used to modify Pt disk for the development of a non-enzymatic electrochemical glucose sensor. The prepared Pt/CuO sensor showed sensitivity in alkaline media for electrochemical glucose sensing, which is promising to be an excellent non-enzymatic glucose sensor.

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2. Experiments

2.1 Hydrothermal synthesis of CuO nanoplates

CuO nanoplates were synthesized by a simple hydrothemal method without using any surfactant. In a typical process, 2.4 g $CuCl_2$ and 1.7 g KOH were dissolved in 80 mL of deionized water (DI) using a magnetic stirring for about 20 min at room temperature. The mixed solution was transferred into a Teflon-lined autoclave (100 mL in volume) for hydrothermal treatment at 180 °C for 23 h. The resulted products were washed five times with DI water and collected with ethanol solution by centrifugation at 4000 rpm for 15 min. Finally, the collected products were dried at 60 °C for 20 h. The morphologies and crystal structures of the as-synthesized materials were characterized by field-emission scanning electron microscopy (FESEM, JEOL 7600F) and power X-ray diffraction (XRD; Advance D8, Bruker) respectively.

2.2 Fabrication of CuO nanoplates modified Pt grid

In a typical process, 0.14 g CuO was mixed with 0.02 g polytetrafluoroethylene (PTFE) and crushed in an agate mortar. The mixed composition was compressed under a pressure of 9800 kPa to form a round disk of 1 cm in diameter. The CuO nanoplates modified Pt grid was obtained by compressing the round disk to a Pt grid.

2.3 Non-enzymatic glucose measurement with the electrochemical method

The glucose measurement was performed at room temperature by using the PGSTAT30 Autolab electrochemical workstation (Eco Chemie, Netherlands). Three electrodes were used: reference electrode (Ag/AgCl, Metrohm), counter electrode (Pt), and the working electrode (Pt/CuO nanoplates). Cyclic voltammograms (CV) were performed in NaOH 0.1M with potential from -0.6 to 0.8 V until reproducible background voltammograms were obtained. Non-enzymatic glucose measurement was carried out in 0.1M NaOH at the potential from 0 to 0.7 V at a scan rate of 50 mV/s.

3. Results and discussion

3.1 Characterization of CuO nanoplates

Fig.1 shows the FE-SEM images of CuO nanostructures synthesized using the hydrothermal method. As shown in Fig.1, nanoplates were formed with the width, length, and thickness of 0.9 ± 0.08 μm, 1.76 ± 0.15 μm, and 70 ± 4 nm respectively.

The XRD pattern of the fabricated CuO nanoplates is shown in Fig.2. All typical diffraction peaks can be readily indexed to the monoclinic structure of CuO (JCPDS PDF card No. 05-0611). The major peaks located at 2θ = 35.5° and 38.7° are indexed as (002) and (111) crystal planes, respectively. Except for CuO, no other peaks were observed in the pattern, which verified that the synthesized nanostructures were pure CuO.
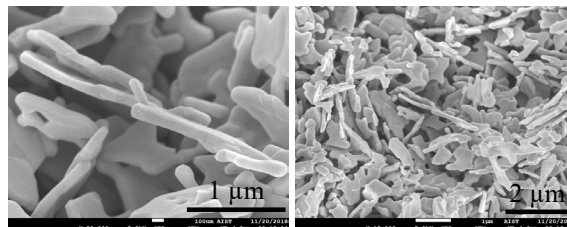

Fig. 1. FE-SEM images of CuO nanostructures were synthesized by the hydrothermal method at 180 °C for 23 h.
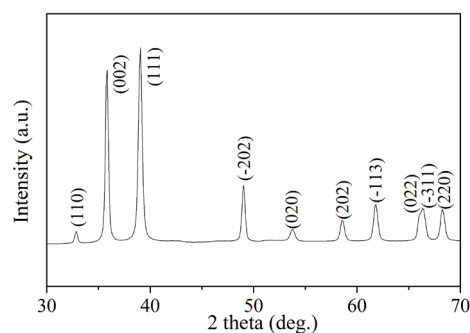

Fig. 2. X-ray diffraction patterns of CuO nanomaterials fabricated by hydrothermal synthesis at 180 °C for 23 h.
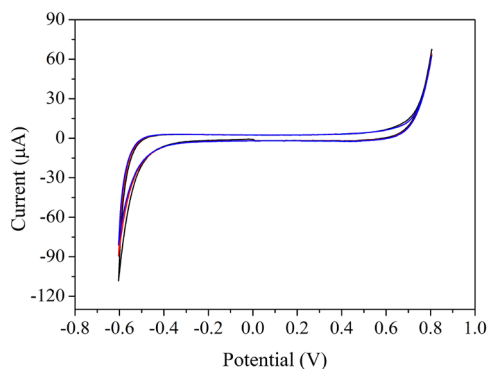

Fig. 3. CV of Pt working electrode in NaOH 0.1M with potential from -0.6 to 0.8 V at a scan rate of 50 mV/s.

3.2 Glucose measurement using cyclic voltammetry

Before glucose measurement, cyclic voltammograms (CV) of Pt working electrode were performed in NaOH 0.1M with potential from -0.6 to 0.8 V until reproducible background voltammograms were obtained (Fig.3). As shown in Fig.3, hydrogen evolution and oxidation reactions started at -0.4 and

0.7 V respectively. The windown potential in this experiment is from -0.4 V to 0.7 V. In the current experiments, we aim to detect glucose oxidation reaction, the potential range from 0 to 0.7 V was selected for further experiments.
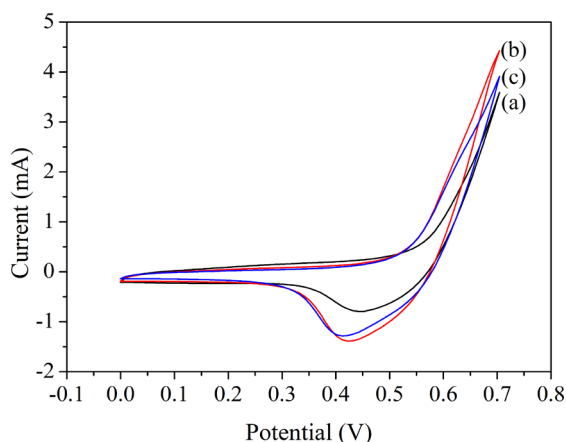

Fig. 4. CV of CuO nanoplates in NaOH 0.1M in the presence of (a) 0 M glucose, (b) 0.1 mM glucose, and (c) 2 mM glucose at a scan rate of 50 mV/s.
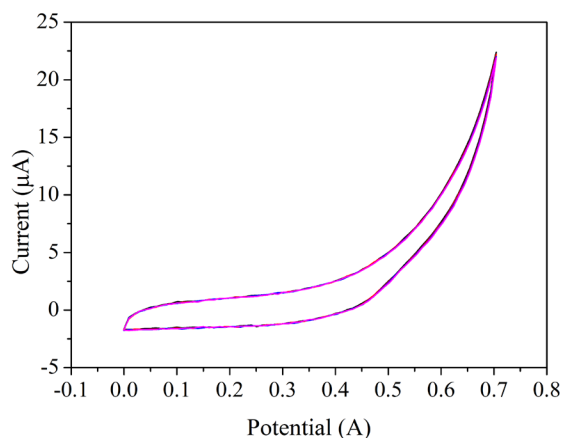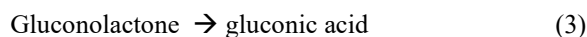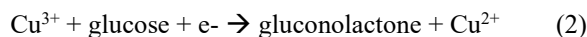

Fig. 5. CV of Pt electrode in NaOH 0.1M in the presence of 2 mM glucose.

The cyclic voltammetry was applied to the Pt/CuO nanoplates electrode to measure glucose concentration in NaOH 0.1M at 50 mV/s (Fig.4). As shown in Fig.4a, when glucose was not added to the electrolyte solution, no oxidation peak was observed. When 0.1 mM glucose was added to the electrolyte solution, the oxidation peak at 0.65 V was found (Fig.4b). The oxidation peak was clearer when glucose concentration was increased to 2 mM (Fig.4c). Similar results were found in the research of Rahim et al. [15] when measuring glucose with SiO_2/C/CuO working electrode.

In order to verify the role of CuO nanostructures in glucose oxidation, the cyclic voltammogram was performed with Pt electrode in NaOH 0.1M in the presence of 2 mM glucose. As shown in Fig.5, no glucose oxidation peak was observed. This result confirms the role of CuO nanostructures as electrocatalytic oxidation of glucose in an alkaline medium. The double bond between the copper and oxygen atoms facilitates the electron transfer from the electrode surface to glucose [13].

The mechanism for electrocatalytic oxidation of glucose by CuO nanostructures can be divided into three steps as shown in Scheme 1 [4][13]. In the first step, the CuO is electrochemically oxidized to strong oxidizing agent Cu^{3+} species when it is diffused to the electrode surface (Equation 1). The Cu^{3+} oxidizes glucose to form gluconolactone in the second step (Equation 2), which can be easily transformed into gluconic acid in an aqueous medium in the third step (Equation 3).

$$Cu^{2+} + OH^- \rightarrow Cu^{3+} + e^- \qquad (1)$$

$$Cu^{3+} + glucose + e^- \rightarrow gluconolactone + Cu^{2+} \qquad (2)$$

$$Gluconolactone \rightarrow gluconic\ acid \qquad (3)$$

Scheme 1. The mechanism for electrocatalytic oxidation of glucose by CuO nanostructures.

CuO nanoplates fabricated with the hydrothermal method can be used to detect glucose with concentration as low as 0.1 mM by electrochemical method. This value is much smaller than the allowed blood glucose level (3.8 to 5.1 mM). However, the response signal is still quite small as compared to previous research based on electrochemical detection of glucose on different CuO nanostructures [7][10]. Functionalization of CuO nanoplates by some materials such as carbon nanotube, graphene, or other metals may help to increase the sensitivity of the sensor.

4. Conclusion

CuO nanoplates have been successfully fabricated using the simple hydrothermal method at 180 °C for 23 h without using any surfactant. The as-fabricated CuO nanoplates were mixed with PTFE and compressed to Pt grid to form Pt/CuO nanoplates working electrode for electrochemical experiments. Cyclic voltammetry was performed on the Pt/CuO nanoplates electrode with potential from 0 to 0.7 V in NaOH 0.1M to detect glucose. The oxidation peak of glucose was found at 0.65 V with a concentration as low as 0.1 mM. The role of CuO nanostructures as electrocatalytic oxidation of glucose in alkaline medium was verified. The results show that CuO nanoplates are promising materials for glucose detection. The functionalization of CuO nanoplates may improve the sensitivity of the glucose sensor.

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