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Photoactive and self-cleaning properties of copper oxide thin film non-enzymatic glucose biosensor

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ABSTRACT

In this study, CuO thin film has been prepared using a solution deposition process for the non-enzymatic electrocatalytic oxidation of glucose. The structure of the CuO was analyzed using X-ray diffraction technique while its electrocatalytic performance was investigated using cyclic voltammetry and chronoamperometry. The as-prepared CuO electrode exhibited a good response towards the oxidation of glucose due to its excellent electrocatalytic activity and electron transfer ability. In addition, the electrode demonstrated a good photocatalytic and self-cleaning ability during and after its exposure to light. These satisfactory performances make the electrode material promising for the development of effective non-enzymatic glucose sensors. In addition, the simple and low-cost fabrication procedure can be used to prepare electrodes on a large scale.

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1. Introduction

The development of glucose sensing devices which are low-cost, less complicated and highly sensitive has been the focus of researchers in the recent times due to their significance in medical diagnosis and treatment as well as in key areas such as food and nanotechnology [1]. Earlier on, efforts have been concentrated on the advancement of sensors based on glucose oxidase enzyme. Contrariwise, enzyme-based glucose sensors are limited due to inadequate long-term stability, poor reproducibility and cost-intensiveness [2]. In addition, they are mostly based on sophisticated processes and are vulnerable to prevalent environmental conditions such as temperature, humidity and pH [3]. Thus, the attention of investigators has been drawn to the development of non-enzymatic glucose detection devices with enhanced electrocatalytic performance, selectivity and sensitivity. As a result, emphasis is currently being placed on the synthesis of electrodes from metals and metal oxides, as well as material composites.

Several metals such as Ni, Ag, Au and Pt and metal oxides including TiO_2, ZnO, CuO, NiO, SnO_2, CO_3O_4, MnO_2 and Cu_2O [4–6] have been used for the production of new glucose sensors. Specifically, copper oxide (CuO), an attractive auspicious noble metal oxide belonging to the monoclinic crystal family has been extensively used in diverse fields for multiple applications. This low-priced transition metal oxide is utilized for several advanced applications ranging from supercapacitors, photo-electrochemical sensors, gas sensors, high temperature semiconductors, catalysis, lithium-ion batteries and in the innovative production of antimicrobial agents and memristors [7]. The widespread usage of CuO is not implausible, as it is freely available and affordable. Besides, its characteristic physical and chemical properties make it a unique compound highly sought for [8]. CuO-based electrodes have been reported as excellent non-enzymatic glucose sensors owing to their exceptional electrochemical activities, outstanding chemical stability, and increased precise surface area [9]. Additionally, CuO nanomaterials have the advantages of existing in different sizes, structures and morphologies which improve the electrochemical behavior of the developed electrode by enlarging the surface area. The self-cleaning ability of CuO has nurtured its use as biomedical devices coatings and as separation sheaths [10].

However, to the best of the authors' knowledge, there is limited information detailing the photo-activity and self-cleaning electrochemical behaviour characterizing CuO thin film glucose biosensors when exposed to light. In this study, we report a solution deposition process of fabricating CuO thin film onto FTO (Fluorine-doped Tin Oxide) glass slide by a two-step spin coating

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method. The as-prepared CuO electrodes demonstrated a good response to glucose oxidation due to its outstanding electrocatalytic behaviour and enhanced transference of electrons. Furthermore, the CuO electrode exhibited good photocatalytic and self-cleaning properties upon its exposure to light. The foregoing properties make the developed CuO nanoparticles a promising electrode material for non-enzymatic glucose detection. Moreover, the cost-effectiveness and uncomplicated means of fabrication used in this study could produce large scale electrodes very expeditiously.

2. Methodology

2.1. Materials and methods

Sodium hydroxide pellets (NaOH), copper(II) chloride dihydrate ($CuCl_2{\cdot}2H_2O$), nickel chloride ($NiCl_2$), sodium oleate d-(+)-glucose, ascorbic acid (AA), acetaminophen (AC), uric acid (UA), fructose ($C_6H_{12}O_6$), hexane, ethanol (C_2H_5OH), toluene ($C_6H_5CH_3$) were obtained from Sigma Aldrich South Africa. These chemicals were used as received without additional purification. Deionized water was used for the preparation of all the aqueous solution used.

2.2. Electrode fabrication

The process used in synthesizing the copper oleate has been previously reported by Wang and co-workers [11]. The CuO nanocomposite film was produced on FTO glass slide using a solution deposition technique which was followed by a two-stage spin coating process. The fabrication process involved thorough cleaning of the cut FTO glass slides with mucasol detergent in ultrasonic bath for 10 mins. Afterwards placing them for another 10 mins in ethanol in the ultrasonic bath and finally in water in the ultrasonic bath for a further 10 mins. The cleaned glass slides were air dried with an electric air pump and inserted into an oven at 60 °C.

A mixture of 3.409 g copper(II) chloride dihydrate and 18.27 g of sodium oleate were mixed with ethanol and hexane. An amount of 0.09 g of copper oleate was then circulated in a vial containing 500 µL of toluene. The combined solution was sonicated for about 45 mins to obtain homogenous solution. 50 µL of the solution was spin coated on the 1 cm^2 area of the pre-cleaned conductive FTO glass at 2500 rpm for 30 s and 4000 rpm for 60 s consecutively to enhance uniform coating distribution of the thin film. The coated glass was calcined at 350 °C for 10 min. Four layers were repeated based on preliminary experiments confirming four-layered film as the optimal thickness with the best electrochemical characteristics. The two previous steps were repeated accordingly, with different conductive glass substrates. All the electrodes were calcined at 350 °C for 4 h once the fourth layer was reached. The electrodes were cooled to an ambient temperature before being vacuum sealed for experimental analysis.

2.3. Surface characterization of the electrode

The crystal structure of the electrode was identified with the aid of an X-ray diffraction (XRD). The XRD patterns were analyzed using a PANalytical X'Pert PRO PW3040/60 X-ray diffractometer with a Fe filtered Cu-Kα (λ = 0.154 nm) monochromated radiation source.

2.4. Electrochemical measurements and characterization of the electrode

Cyclic voltammetric (CV) and chronoamperometric (CA) measurements were conducted at room temperature in 100 mL of 0.1 M NaOH contained in an electrochemical cell using an Autolab PGSTAT302N potentiostat (Metrohm., Switzerland). Three-electrode system was set up with Ag/AgCl/KCl (3 M) as a reference electrode, carbon rod as a counter electrode and the prepared FTO-CuO electrode as a working electrode. The chronoamperometric response was obtained at 0.55 V following the addition of various glucose concentrations in 0.1 M NaOH solution at 30 s time interval under continuous stirring to attain a homogenous solution while measuring the corresponding currents.

The photo-induced electrochemical analyses were carried out using a 7 W white light bulb operating at 10 V as the source of lighting. The light current signal was regulated on a computer-controlled Autolab PGSTAT302N potentiostat (Metrohm., Switzerland).

3. Results and discussion

3.1. Surface evaluation of the electrode

The CuO phase present in the CuO thin film prepared on the FTO substrate was analyzed using XRD and the results are presented in Fig. 1. In the diffraction spectra, the peaks marked with red dots correlate with those of the CuO crystallites [12] while the peaks designated with black dots are for the FTO glass. The diffraction patterns of the as-prepared CuO electrode showed that the thin film contains CuO structure even though its intensity is much lower compared to the FTO substrate. This could be as a result of the thinness of the developed film which is in contrast with the thickness of the FTO glass. The CuO diffraction peaks become visible at about 31.72°, 36.36°, 37.98°, 54.56°, 56.34° and 61.70° matching with (110), (002), (111/200), (−020), (202) and (−113) respectively. These diffraction peaks are consistent with distinct planes of monoclinic CuO phases [13]. The observed peaks agree with JCPDS Ref. 045-9537 and JCPDS Ref. 80-0076.

3.2. Electrochemical properties of the electrode

The response of the as-prepared CuO electrode to the detection of glucose was analyzed using cyclic voltammetry. With the addition of 1 mM of glucose in 0.1 M NaOH solution at a scan rate of 25 mVs^{-1}, it was clearly visible from the CV measurements that there was a wide oxidation peak detected within 0.5–0.6 V vs Ag/AgCl. However, there was no evidence of any oxidation peak in the

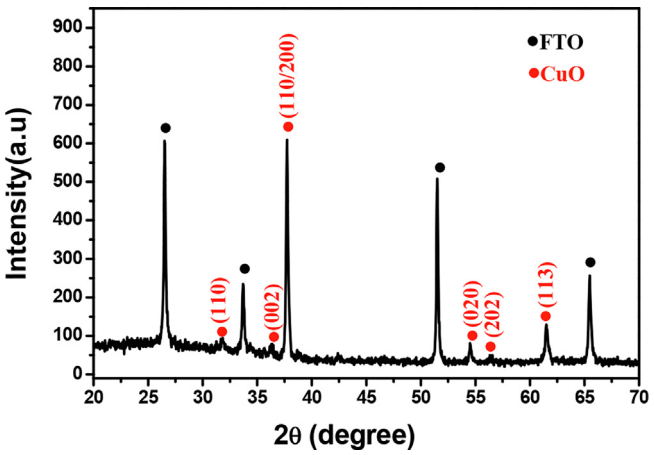

Fig. 1. XRD patterns of the FTO-CuO electrode showing the diffraction peaks for the CuO crystallite (red) and the FTO glass (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

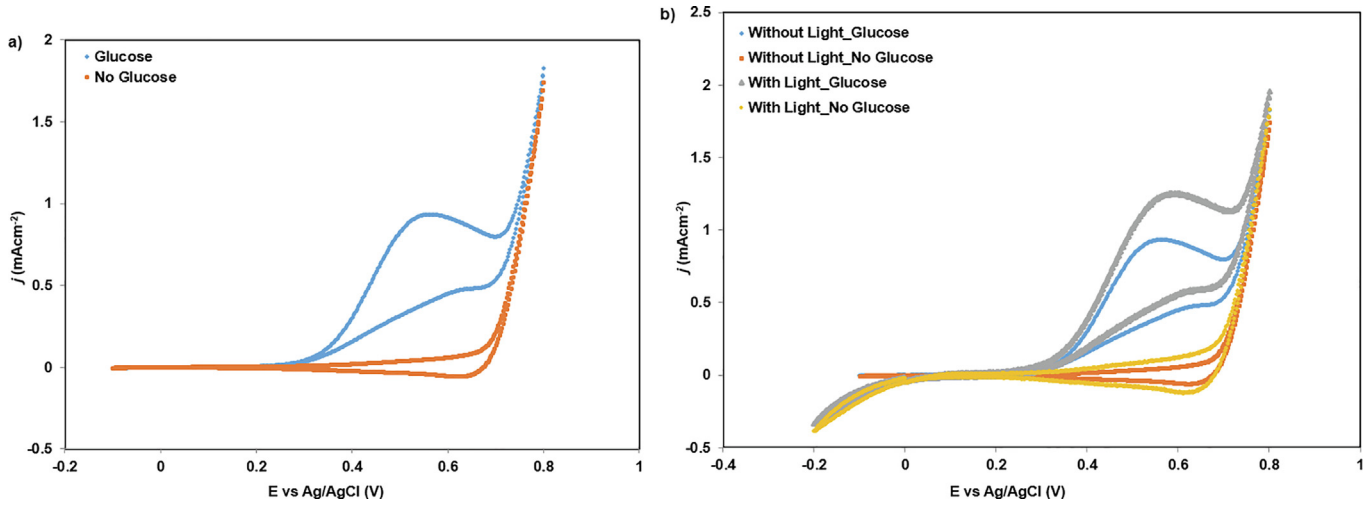

Fig. 2. Electrochemical behaviour of the CuO thin film electrode in 0.1 M NaOH electrolyte solution; cyclic voltammogram of the CuO a) With and without the addition of glucose b) With and without the addition of glucose after exposure to light.

absence of glucose during the CV tests (Fig. 2a). The significant increase in the current is an indication that the CuO possesses excellent electrocatalytic properties which improves the detection ability of the CuO nanoparticles (Fig. 2a). Furthermore, the rise in the oxidation potential could be due to the conversion of copper (II) to copper (III) in alkaline medium (Eq. (1)). The oxidation of glucose took place in an alkaline medium of 0.1 M NaOH (50 mL NaOH) over the CuO nanoparticles to produce gluconic acid. The mechanism by which glucose is oxidized on the electrode can be illustrated as shown in the following equations [14].

$$CuO + OH^- \rightarrow CuO(OH) + e^- \quad (1)$$

$$2CuOOH + e^- + \underset{\text{Glucose}}{(C_6H_{12}O_6)} \rightarrow 2CuO + \underset{\text{Gluconolactone}}{(C_6H_{10}O_6)} + 2H_2O \quad (2)$$

It has been reported that during the electro-oxidation reactions of glucose to gluconolactone (Eq. (2)), copper (III) has the affinity for transferring electrons that is produced. Similar occurrences have been described in literature [15]. The photocatalytic activity of CuO is evident when studying the effect of exposing the electrode to light during the CV experiment (Fig. 2b). A considerable increase in the peak oxidation current was observed while carrying out the glucose detection experiment under light compared to that performed without light (Fig. 2b). Moreover, a clear distinction was seen when the testing was carried out in blank solution (without glucose) in the presence and absence of light (Fig. 2b) which further corroborates the photoactive behaviour of the synthesized CuO electrode.

3.3. Chronoamperometry study of the electrode

Chronoamperometry is a very responsive electrochemical method of characterizing biosensors. The response of the CuO electrode was examined in the presence and absence of light to the successive glucose addition in 0.1 M NaOH solution at an applied potential of 0.55 V. The potential was selected since the oxidation peak obtained from the CV is within the potential range of 0.5 V and 0.6 V. Also, the reaction of the electrode in blank solution (without glucose) was studied amperometrically. The electrolyte was constantly stirred during the testing, whether exposed to light or not. In Fig. 3a, the amperograms with and without glucose addition were compared. Under light, the CuO electrode attained a current of 3.20 μA at +0.55 V versus Ag/AgCl. Meanwhile, a lower corresponding current of 2.38 μA was recorded in the absence of light (Fig. 3a). With the introduction of glucose to the electrolyte,

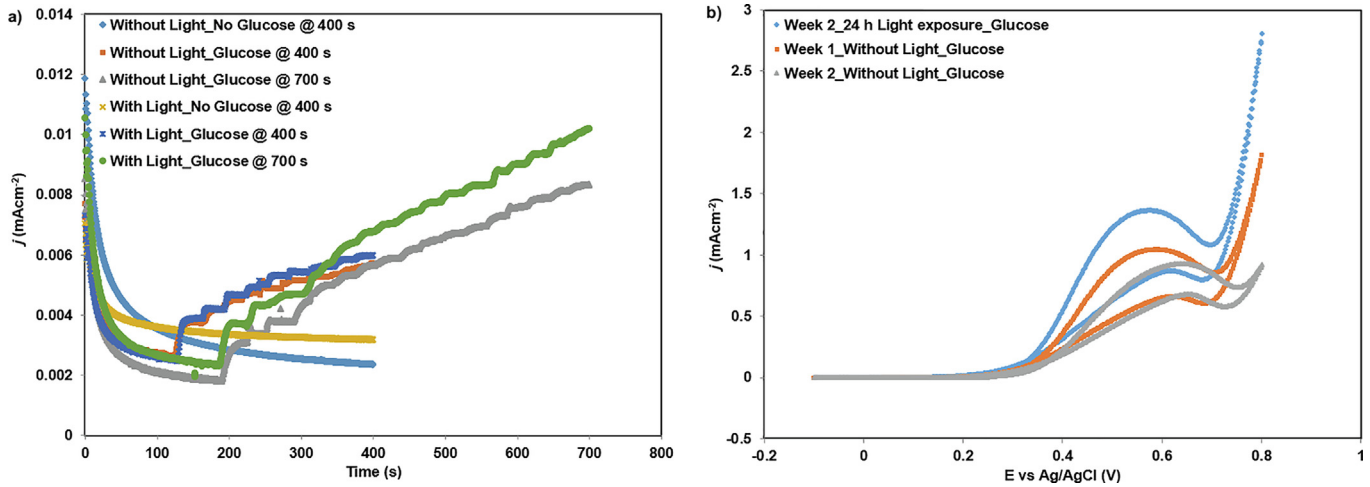

Fig. 3. a) Chronoamperometry of the CuO electrode with and without glucose, before and after exposure to light b) CV showing self-cleaning ability of the CuO electrode after 24 h exposure to light.

within the same time interval, the illuminated CuO electrode showed a higher current response to the successive addition of glucose, a current of 6.01 μA and 5.68 μA were obtained with and without light respectively. Moreover, with further addition of glucose, at the same applied potential of 0.55 V, the current response recorded at 700 s, with and without irradiation was 10.18 μA and 8.34 μA respectively (Fig. 3b). The efficiency of the CuO nanoparticles was enhanced through illumination resulting in increased electron transfer. These findings are consistent with results reported from a previous study [16].

Another characteristic of the developed sensor that requires additional investigation is its self-cleaning potentiality. In order to verify this property, CuO electrode was tested. After the electrode had been used for the determination of glucose (week 1), it was washed with deionized water and kept at room temperature. After a week (week 2), the same electrode was used for glucose detection, and the corresponding CV showed that it has lost about 11% of its initial oxidation peak current (Fig. 3b). This shortfall in the current response may be due to contaminants, such as glucose oxidation fragments which destroys the stability and shelf life of the fabricated electrode. In order to establish the self-cleaning properties of the sensor, the CuO electrode was washed with deionized water and irradiated under natural light for 24 h at room temperature. As a result of its exposure to light, the electrode was able to fully recover back its initial oxidation peak current, in fact an appreciably higher peak current was recorded. This observation necessitates further studies in order to ascertain and establish the practical applicability of the as-prepared CuO electrode.

4. Conclusions

In this study, we fabricated CuO thin film for the detection of glucose using a simple deposition method. The CuO electrode demonstrated a satisfactory electrochemical response toward glucose oxidation confirming its excellent electrocatalytic activity and electron transfer ability. In addition, the electrode displayed a good photocatalytic and self-cleaning ability when exposed to light. Our findings make the electrode material promising for the development of low-cost non-enzymatic glucose sensors.

CRediT authorship contribution statement

Adijat O. Inyang: Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing. **Mahabubur Chowdhury:** Conceptualization, Methodology, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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