Journal of Colloid and Interface Science 493 (2017) 349–355

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

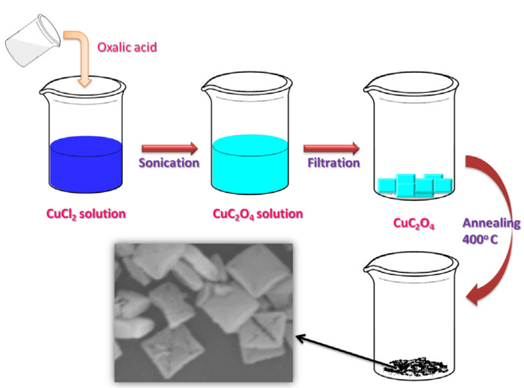
Synthesis and characterizations of biscuit-like copper oxide for the non-enzymatic glucose sensor applications

Murugan Velmurugan, Natarajan Karikalan, Shen-Ming Chen *

[a] *Electroanalysis and Bioelectrochemistry Lab, Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao East Road, Taipei 106, Taiwan, ROC*

GRAPHICAL ABSTRACT

Synthesis route for the preparation of biscuit-like copper oxide by precipitation cum thermal annealing process.



ARTICLE INFO

Article history:
Received 26 October 2016
Revised 11 January 2017
Accepted 12 January 2017
Available online 16 January 2017

Keywords:
Copper oxalate
Copper microstructures
Human serum
Glucose analysis
Screen printed carbon electrode

ABSTRACT

We described the synthesis of biscuit-like copper oxide (CuO) by the precipitation cum thermal annealing process. The biscuit-like CuO microstructures were successfully obtained by template free synthesis process. Thereby, the oxalic acid was used as the shape forming agent. Herein, the role of the sonic wave was quite important to controlling the shape. The CuO microstructures were characterized by the X-ray diffraction pattern, scanning electron microscope and energy dispersive X-ray analysis. The as-prepared CuO was used to fabricate the disposable sensor electrode using screen printed carbon electrode (SPCE). The CuO modified SPCE was successfully determined the glucose with the linear concentration ranging from 0.0005 to 4.03 mM and the lowest detection limit of 0.1 µM. The biscuit-like CuO microstructures based glucose sensor displayed appreciable analytical performance than the other CuO nanostructures. Moreover, the disposable CuO/SPCE was applied to determine the glucose in human blood serum, saliva and urine samples. The developed glucose sensor attained good recoveries in real sample analysis, hence, it is applicable for the commercial applications.

* Corresponding author.
E-mail address: smchen78@ms15.hinet.net (S.-M. Chen).

http://dx.doi.org/10.1016/j.jcis.2017.01.044

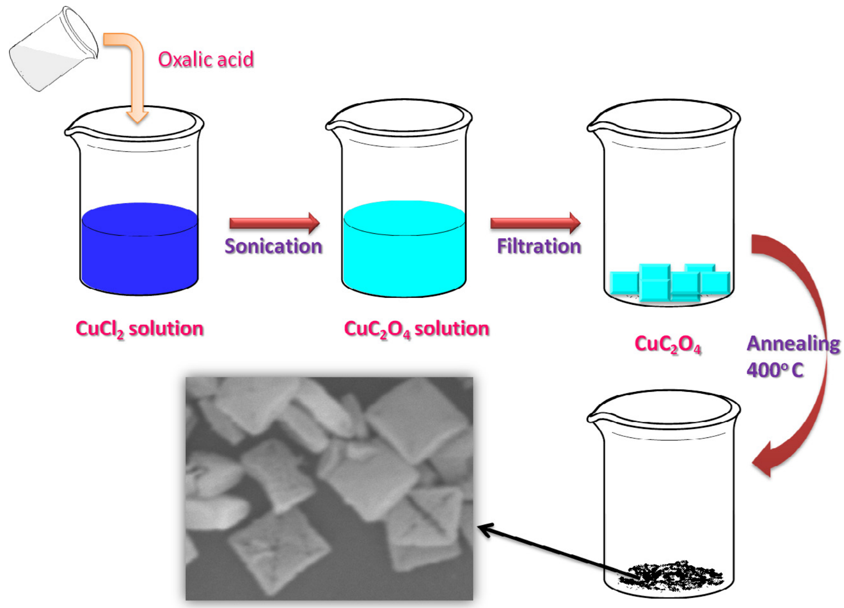


Fig. 1. The schematic view of the synthesis procedure for the preparation biscuit-like CuO.

1. Introduction

CuO is a p-type semiconductor and has a narrow band gap of 1.2 eV, which is widely used as a promising electrode for the reduction of carbon dioxide. Besides, CuO has been used in gas sensors, biosensors, photocatalysis, lithium ion electrode materials, magnetic devices and solar cells [1–4]. Hitherto, many recent studies has been reported a variety of CuO nanostructures which including nanocubes [5] nanorods [6], nanowires [7], nanoneedles [8], nanoribbons [9], nanoplatelets [10], sheaf-like CuO [11], flowerlike CuO [12], nanocages [13], hollow CuO microspheres [14], sheet-like and urchin-like CuO [15]. All the aforementioned nanostructures are synthesized by the template assistant method. Hence, the growing material science needs an efficient and promising route to prepare nanomaterials. Commonly, the precipitation cum thermal decomposition method manifested nanostructured CuO with definite shape [16]. This nanostructured CuO could be applied to the determination of non-enzymatic glucose.

The glucose is an important compound for living organisms, however the increase of glucose concentration directs the human to diabetes mellitus [17]. Diabetes mellitus is a group of metabolic disorder, particularly, it causes cardiovascular disease and eye damage [18]. Thus, the determination of glucose concentration in the blood is necessary for the routine physiological fitness. So far, numerous methods have been reported to determine the glucose such as electronic, fluorescent, optical, acoustic, transdermal and electrochemical methods [19–24]. Among them, the electrochemical determination is rapid, cost effective and applicable to the miniature devices. Usually, the commercial electrochemical glucose sensor based on the glucose oxidase enzyme. Wherein, the glucose molecule was reacted with saturated oxygen in blood and produces the hydrogen peroxide (H_2O_2) [25]. Further, the H_2O_2 was reduced by the other mediators and produced a tiny amount of current changes. This current response was calibrated to estimate the concentration of glucose [26]. Conversely, the enzymatic glucose sensors have some limitations, which arise by the temperature, pH, oxygen and humidity [27]. Therefore, the non-enzymatic glucose sensor was developed for the alternative to enzymatic glucose sensors.

In past decades, several non-enzymatic glucose sensors have been reported based on the noble metals (Pd, Pt and Au). However, the low abundance especially the high costs of noble metals are further avoided [28]. Though, numerous non-enzymatic glucose sensors were fabricated by the transition metals and its derivatives. For instance, the transition metal compounds are Co, Ni, Cu, Co_3O_4, WO_3, NiO, TiO_2, MnO_2, CdO/CuO, Mn_3O_4, Fe_2O_3 and ZnO, etc [29]. Among all transition metals, the nickel and copper have received a great interest due to their exclusive redox behavior [30]. As mentioned earlier, there are varieties of nanostructure reported for the copper based compounds. In contrast with nickel, the copper provides high sensitivity, selectivity and low potential oxidation towards the glucose determination. Herein, we report the simple synthesis route for the preparation of biscuit-like CuO by the precipitation cum thermal annealing process. The as-prepared compound was scrutinized by various physicochemical characterizations and analytical measurements. The CuO was modified on SPCE and used as the disposable sensor electrode. The CuO/SPCE was successfully applied to the determination glucose in real samples and achieved good recoveries. The developed CuO/SPCE glucose sensor electrode was compared with the other copper oxide nanostructures and examined the analytical parameters.

2. Experimental section

2.1. Materials

The SPCE (working area = 0.07 cm^2) was purchased from Zensor R&D Co., LTD, Taiwan. Copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$), oxalic acid, fructose, sucrose, galactose, lactose, H_2O_2, uric acid (UA), ascorbic acid (AA), dopamine (DA) and NaOH were purchased from Sigma-Aldrich, Fluka and Wako chemicals and used as-received without any further purification.

2.2. Apparatus and electrochemical measurements

The structure of the CuO was investigated by X-ray diffraction pattern analysis (XRD), XPERT-PRO (PANalytical B.V., The Netherlands) with CuKα radiation (λ = 1.5406 Å). The surface morphology and the elemental composition of CuO were analyzed by scanning electron microscope (SEM) Hitachi S-3000 H attached with energy dispersive X-ray analyzer (EDX). All the electrochemical studies