



Facile wet-chemical synthesis of differently shaped cuprous oxide particles and a thin film: Effect of catalyst morphology on the glucose sensing performance

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ABSTRACT

In this work, different facile synthesis routes were developed to create cuprite-based catalyst systems for the amperometric detection of glucose, allowing us to evaluate the impact of important electrode fabrication parameters on the glucose sensing performance. Using homogenous precipitation routes based on a redox system, two differently shaped cuprite particles—skeletons and polyhedrons—could be obtained. Furthermore, a novel electroless deposition technique was introduced that does not require sensitization and activation pretreatments, allowing for the direct modification of the glassy carbon. This technique produced electrodes with dense thin film consisting of merged, octahedral cuprite crystals. Afterward, these materials were tested as potential catalysts for the electrochemical detection of glucose. While the catalyst powders obtained by precipitation required Nafion[®] to be attached to the electrode, the thin film synthesized using electroless plating could be realized with and without additive. Summarizing the results, it was found that Nafion[®] was not required to achieve glucose selectivities typically observed for cuprite catalysts. Also, the type of catalyst application (direct plating vs. ink drop coating) and the particle shape had a pronounced effect on the sensing performance. Compared to the thin film, the powder-type materials showed significantly increased electrochemical responses. The best overall performance was achieved with the polyhedral cuprite particles, resulting in a high sensitivity of 301 $\mu\text{A mmol}^{-1} \text{cm}^{-2}$, a linear range up to 298 $\mu\text{mol L}^{-1}$ and a limit of detection of 0.144 $\mu\text{mol L}^{-1}$.

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1. Introduction

In 2013, the World Health Organization published recent figures on persons suffering from diabetes. According to this report, over 347 million persons are afflicted with hyperglycemia and therefore need a continuous and accurate control of their blood sugar level by using a handy and reliable monitoring system [1]. Since the first establishment of an enzyme-based glucose sensor by Clark and Lyons in 1962, further improvements have led to three generations of blood glucose devices [2].

Nowadays, most commercially available biosensors are based on the glucose oxidase principle. However, these systems exhibit

some disadvantages such as low stability, high cost of enzyme material and a complex immobilization process. Consequently, the demand for the development of new and suitable non-enzymatic electrocatalytic active electrodes has arisen in recent decades. New laboratory research on the topic involves the use of noble metals such as gold (Au) [3], platinum (Pt) [4], and alloys thereof [5,6]. However, these electrodes occasionally suffer from low selectivities, high costs and poisoning.

Some investigations also have been carried out with copper and its oxides, based on intensive studies of their intrinsic activity and the conversion mechanism [7,8]. In general, the usage of cuprite (Cu_2O) benefits from its low oxidation potential in alkaline solutions that consequently leads to enhanced sensitivities compared to more noble metals, although the stability of the material lacks in acidic media.

Many publications describe the synthesis of copper oxide materials with different sizes and morphologies, such as cubes and spheres, and the application of these materials in the

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electrochemical detection of glucose [9–11]. However, most of these studies remain restricted to a single or few closely related catalyst types [12–14]. For example, the sensing performance of cuprite/copper octahedron in micrometer scale was evaluated according to [9]. In another publication, Reitz et al. described the synthesis of copper oxide microspheres with high surface areas [11]. Furthermore, the group of Zhang et al. presented the fabrication and characterization of a multiwalled carbon nanotube/cuprite network in 2012 [14]. On the other hand, Won and Stanciu compared four different types of catalyst morphologies, namely cubes, octahedron, truncated octahedron and hexapods [10]. Such kind of comparative work is important to obtain a basic understanding of the effect of catalyst morphologies and electrode preparation techniques on the sensing performance.

Commonly, electrodes for the detection of glucose are prepared by using catalyst powders in combination with Nafion® as an adhesive additive [11,13–15]. Several papers claim that, in addition to stabilizing the catalyst, Nafion® also is responsible for the catalyst selectivity, as it might repulse negatively charged, possibly interfering species such as ascorbic acid due to electrostatic forces [13–15]. However, in these studies, no reference experiments without Nafion® were performed, which would be required to clearly describe the role of this additive.

In order to obtain cuprite particles with a specific morphology, different methods have been carried out (e.g., hydrothermal [16], sol–gel and electrodeposition techniques [17]). Wet-chemical methods possess many advantages due to low costs and feasibilities. Here, an accurate control of kinetic and thermodynamic parameters is one of the key considerations. Crucial factors include temperature, template agents such as surfactants, and concentration of the used chemicals. During the last few years, several studies focusing on diverse wet-chemical cuprite particle synthesis have been mostly based on the introduction of form-shaping agents [18].

Herein, we report two possible low-cost and easily-realizable routes for the shape-controlled synthesis of cuprite particles leading to well-defined shapes and without the need of form-shaping chemicals. The synthesis is carried out in aqueous solution under mild conditions and with α -D-glucose as reducing agent. We show that, depending on the reaction time and the concentration ratio, it is possible to obtain different structures, namely skeletal and polyhedral particles. In this connection, we compare the effect of catalyst morphology to the glucose sensing performance.

Furthermore, we present a novel cuprite electroless deposition technique whereby the surface of the electrode is directly coated without the need of any pretreatment steps. The adhering films obtained with this method allow us to analyze the performance of well-defined cuprite catalysts in the electro-oxidation of glucose in the absence of Nafion®. Although the obtained results of the sensing performance need to be improved in further studies, we herein present a basic concept for the design of future glucose electrodes by a direct electroless deposition method yielding to higher surface areas.

2. Materials and methods

2.1. Particle preparation

Wet-chemical particle preparation was conducted by using the Fehling method [19]. An aqueous solution consisting of 12 mmol L^{-1} CuSO_4 (copper sulfate, Fluka purum p.a.), 14 mmol L^{-1} $\text{KNaC}_4\text{H}_4\text{O}_6$ (potassium sodium tartrate, Sigma Aldrich) and $175.01 \text{ mmol L}^{-1}$ NaOH (sodium hydroxide, Sigma Aldrich) was heated to 90°C (Fehling I and II). Afterward, a solution (Fehling III) consisting of 4 mmol L^{-1} $\text{C}_6\text{H}_{12}\text{O}_6$ (α -D-glucose, Sigma Aldrich) was added in the same volume ratio of Fehling I + II and Fehling III: 1:1. Using this concentration composition, skeletal particles could

be obtained. In the case of the preparation of polyhedral particles, the concentration of potassium sodium tartrate was increased to 28 mmol L^{-1} , which yielded a concentration ratio of copper sulfate and potassium sodium tartrate of approximately 1:2.

The reaction time was fixed to 60 min for the preparation of skeletal particles and 120 min for the synthesis of polyhedron structures at a constant temperature of 90°C .

Afterward, the obtained precipitation, indicated by a brick-red color, was collected, filtrated and washed several times with ultra-pure water and then dried at room temperature for two days.

2.2. Electroless thin film plating

For the deposition of shape-controlled Cu_2O thin films, electroless plating was used. The plating solution consisted of 25 mmol L^{-1} CuSO_4 pentahydrate (Fluka purum p.a.), 200 mmol L^{-1} $\text{C}_2\text{H}_4(\text{NH}_2)_2$ (ethylenediamine, Roth, for synthesis) and 450 mmol L^{-1} CH_2O (formaldehyde, Fluka puriss. p.a.). The reaction started as the solution was heated close to boiling. Deposition was indicated by the formation of a light-colored, reddish film on the materials in contact with the heated solution (e.g., carbon and polymer substrates or the glass walls of the beaker used for plating). In contrast to the usual reactivity [20,21], no seeding step was required to initiate electroless plating; the film formation relied on heterogeneous, non-catalyzed nucleation [22]. A plating time of 10 min was applied. In general, the thin film could be removed mechanically (e.g., by the use of a tissue) on smooth surfaces. However, on rough surfaces the adhesion was greatly improved.

2.3. Materials characterization

For the X-ray diffraction (XRD) analysis, electroless plating was performed on polycarbonate foil. After the reaction, the polymer was dissolved with dichloromethane (Roth, $\geq 99.8\%$ IR grade), and the deposit was isolated by centrifugation. Measurements were conducted with a diffractometer STOE STADI ($\lambda_{\text{Mo}} = 0.0709 \text{ nm}$) in θ - 2θ geometry.

The morphology and structure of the cuprite particles and the thin film were characterized by scanning electron microscopy (SEM) by using a high definition XL from Philips in a secondary electron modus of voltages from 15 up to 30 kV.

2.4. Electrode preparation and electrocatalysis

All catalysts were applied on a glassy carbon (GC) electrode of 3 mm diameter. In the case of the particulate catalysts, the electrode was modified by drop-coating with ethanolic particle suspensions, yielding a catalyst loading of approximately 0.8 mg. After drop coating, the catalyst powder was modified with diluted Nafion® (Dupont™, distributed by Ion Power, D520 solution 5% alcohol) solution (1 part Nafion® solution, 120 parts ethanol). Excess solution was carefully removed with tissue paper, and the electrode was left to dry.

For the electrochemical experiments of the thin film, a glassy carbon electrode was used as substrate for deposition. Due to the good adhesion of the film to the electrode in alkaline medium, Nafion® addition was not required, and the cuprite-modified electrode could be directly used for sensing. For reference testing the film was immersed in a diluted Nafion® solution (1 part Nafion® solution, 120 parts ethanol).

All electrochemical measurements were performed in a typical three-electrode assembly (potentiostat: GAMRY Reference 600™) with Hg/HgSO₄ as reference and Ag-net as auxiliary electrode. The electrolyte consisted of 100 mM NaOH. During the electrochemical performances, the solution was continuously rinsed with nitrogen gas. The cyclic voltammetric experiments were carried out

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