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# Facile synthesis of copper oxide nanostructures and their application in non-enzymatic hydrogen peroxide sensing

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## ABSTRACT

In this research, different CuO nanostructures (heart/dumbbell-like and grass-like) were successfully synthesized via simple hydrothermal reactions at 130 °C with different amounts of $Cu(NO_3)_2 \cdot 2.5H_2O$ in 20 mL $H_2O$ and 12 mL $NH_3 \cdot H_2O$ for 6 h in the absence of any additive. The initial amount of $Cu(NO_3)_2 \cdot 2.5H_2O$ was found to be critical for CuO morphology evolution. In addition to morphology study by scanning electron microscopy (SEM) and crystal structure study by X-ray diffraction (XRD), as-synthesized samples were characterized systematically by electrochemical methods including cyclic voltammetry (CV), amperometric detection (*i*–*t*) and electrochemical impedance spectroscopy (EIS). It was found that both heart/dumbbell-like and grass-like CuO nanostructures exhibited good electrochemical performance toward low concentrations of $H_2O_2$. High sensitivity, fast and linear response were achieved, which was mainly due to their large specific surface areas and efficient electron transport in corresponding reactions, making them promising candidates for efficient and precise non-enzymatic detection of $H_2O_2$.

## 1. Introduction

Hydrogen peroxide ($H_2O_2$), a common strong oxidant and an essential intermediate in many biomedical reactions [1], has attracted much attention in recent years. The rapid, accurate and reliable detection of hydrogen peroxide is of great significance in many fields such as clinical treatment [2], food and environment safety [3], chemical reactions [4], and pharmaceutical applications [5]. In the past few decades, many analytical methods for $H_2O_2$ detection have been developed including spectrometry [6], titration [7], fluorescence [8], chemiluminescence [9], and chromatographic techniques [10]. However, these methods are usually expensive, time-consuming, and require professional personnel, which make them less favorable for rapid and cost-effective detection of $H_2O_2$. Therefore, the electrochemical method has been valued in recent years due to its high sensitivity, simple, accurate and fast detection, as well as low cost and ease of operation [11,12]. Enzyme-based electrochemical biosensors were fully studied because of their high sensitivity and excellent selectivity. However, a major drawback of enzyme-based biosensors is the lack of stability and poor reproducibility, which originates from the intrinsic nature of enzymes, i.e. easily damaged either thermally or chemically during biosensor fabrication and testing [13,14].

Recently, many studies have focused on enzyme-free electrochemical biosensors because of their high sensitivity, fast response, low cost, and good stability. Transition metallic nanoparticles [15–17], carbon nanotubes [18], semiconducting metal oxides [19], graphene [20], ordered mesoporous carbon [21] and their composites have been studied extensively due to their large specific surface areas and enhanced catalytic activities, which enable sensitive and fast detection of hydrogen peroxide.

Among them, copper oxide (CuO) nanomaterials, *p*-type semiconductors with a narrow band gap of 1.2 eV, have become a promising candidate for the electrode modification material of non-enzymatic electrochemical biosensors because of their high specific surface area, electrochemical catalytic activity, chemical stability, and high electron transfer features [22]. To date, various CuO nanostructures have been synthesized including nanoflower [19], nanowire [22], nanorod [23], etc., and there exist several papers reporting their application in non-enzymatic amperometric determination of $H_2O_2$. For example, Whang et al. [19] prepared a flower-like CuO nanostructure via chemical oxidation of copper foils under hydrothermal conditions. As-prepared sensors exhibited highly sensitive performance toward $H_2O_2$ under alkaline conditions with a sensitivity of 88.4 $\mu$A/mM cm$^2$ and a detection limit of 0.167 $\mu$M. Zhang et al. [4] synthesized hollow copper oxide particles by the electrospinning method, which demonstrated high

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sensitivity (1746.50 μA/mM cm$^2$), low detection limit (0.022 μM) and wide linear response for the determination of $H_2O_2$. Ping et al. [24] fabricated a novel $H_2O_2$ sensing electrode by mixing graphite powder, ionic liquid $OPPF_6$, and CuO NPs. Due to the combination of excellent catalytic activity of CuO NPs and good conductivity of ionic liquids, the electrode exhibited attractive analytical performance in the detection of $H_2O_2$. Despite efforts in exploring the $H_2O_2$ detection capability of individual CuO nanostructures, there has been a lack of understanding of the precursor–structure–property relationship existing in them, i.e. the microstructure evolution of CuO from different amounts of initial precursors and relevant morphology effects on non-enzymatic amperometric detection of $H_2O_2$. This knowledge gap severely hinders the development of non-enzymatic CuO biosensors for detection of $H_2O_2$.

In this paper, we have fabricated enzyme-free $H_2O_2$ electrochemical biosensing materials based on different CuO nanostructures prepared by varying precursor concentrations in simple hydrothermal reactions without any additive and systematically studied the morphology effects on electrochemical properties of CuO. Enhanced electrochemical performance for $H_2O_2$ determination was obtained on both heart/dumbbell-like and grass-like CuO nanostructures, which was due to their large specific surface areas and efficient electron charge transfer property. All the experimental results demonstrated that as-synthesized heart/dumbbell-like and grass-like CuO modified electrodes exhibited great application potential in electrochemical biosensor devices.

## 2. Experimental

### 2.1. Chemicals and reagents

Hydrogen peroxide solutions (30%) and potassium ferricyanide ($K_3Fe(CN)_6$) were purchased from Fisher Scientific. Nafion (Nf) and potassium chloride were obtained from Sigma–Aldrich. $Cu(NO_3)_2{\cdot}2.5H_2O$, $Na_2HPO_4$, $NaH_2PO_4{\cdot}H_2O$, dopamine (DA), ascorbic acid (AA), uric acid (UA), ammonium hydroxide and sodium chloride were purchased from Alfa Aesar. All reagents were of analytical grade and used without further purification. Phosphate buffer solutions (PBS) were prepared by mixing stock solutions of 0.1 M $Na_2HPO_4$ and 0.1 M $NaH_2PO_4{\cdot}H_2O$ and adjusting the pH value with 0.1 M $H_3PO_4$ or 0.1 M NaOH. Double-distilled water was used for the preparation of buffer solutions. $H_2O_2$ solutions were diluted immediately before the electrochemical measurements.

### 2.2. Fabrication of different CuO nanostructures

In a typical synthesis, 0.048, 0.24 or 0.48 g $Cu(NO_3)_2{\cdot}2.5H_2O$ was first dissolved into 20 mL distilled water under magnetic stirring. After 12 mL of 1 M $NH_3{\cdot}H_2O$ was introduced into each mixture under stirring, the clear solution was transferred into a 40 mL Teflon-lined stainless autoclave. The autoclave was sealed, maintained at 130 °C for 6 h, and then allowed to cool down to room temperature naturally. The obtained black precipitates were washed with distilled water and ethanol several times and then dried in air overnight.

### 2.3. Electrode modification

CuO nanomaterials modified electrodes were fabricated by the following way: a glassy carbon electrode (GCE, $\Phi = 3$ mm) was first polished with a 1700# diamond paper and then washed successively with double-distilled water and ethanol several times; then, 5 μL Nf solution was diluted with 0.7 mL water and 0.3 mL isopropanol to 0.025% (v/v); next, 2 mg CuO sample was dispersed in 1 mL diluted Nf solution and followed by ultrasonication for 2 h; finally, 24 μL of the corresponding suspension (2 mg/mL) was casted on the GCE surface and dried in air. Thus the CuO/Nf modified GCE was obtained. As-prepared modified electrodes were stored in a refrigerator (4 °C) when not in use.

### 2.4. Apparatus and measurements

All the electrochemical experiments were performed on a CHI 650E electrochemical analyzer (CHI, USA) with a conventional three-electrode cell. The working electrode is a bare or modified glassy carbon electrode. An Ag/AgCl and a platinum wire were used as the reference and auxiliary electrodes. 0.1 M KCl was used as supporting electrolyte in a 0.1 M phosphate buffer solution. A magnetic stirrer and a stirring bar were used to provide convective mass transport. Electrochemical impedance spectroscopy (EIS) measurements were performed in 0.1 M KCl solutions within the frequency range of 0.1 Hz to 10 kHz by using 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) mixture as the electroactive probe. The electrolytic solutions were purged with purified nitrogen for at least 30 min before electrochemical measurement. All the experiments were carried out at room temperature.

Crystal structure analysis was carried out by powder X-ray diffraction (XRD) via a Bruker D2 diffractometer at the voltage of 30 kV and current of 10 mA with Cu Kα radiation ($\lambda = 0.15418$ nm), in a $2\theta$ angular range of 20–70° at a scanning speed of 9° min$^{-1}$. Surface morphologies of different CuO nanostructures were observed by a scanning electron microscopy (SEM, FEI Quanta 200) operating at 20 kV and 10 kV respectively.

## 3. Results and discussion

### 3.1. Microstructure characterization of CuO nanostructures

Different morphologies of as-synthesized CuO nanostructures were observed by using SEM and are shown in Fig. 1. All the three samples were prepared under the same hydrothermal conditions except using different amounts of $Cu(NO_3)_2$ (0.048, 0.24, and 0.48 g) as precursors. Fig. 1a shows the CuO nanostructures prepared with 0.048 g $Cu(NO_3)_2$. It is clearly seen that both heart-like and dumbbell-like CuO nanostructures were present, with particle sizes in the range of 2–3 μm. The magnified SEM image in Fig. 1d reveals that the surfaces of the heart-like and dumbbell-like CuO nanostructures were rough and composed of numerous nanoplatelets. The entire architecture of both heart-like and dumbbell-like CuO nanostructures was constructed by incomplete combination of two CuO microspheres that consisted of self-assembled oriented nanoplatelets. After increasing the amount of precursor $Cu(NO_3)_2$ to 0.24 g, a uniformly distributed grass-like CuO nanostructure was observed in the sample as shown in Fig. 1b. From the magnified image of Fig. 1e we can see that the grass-like morphology consisted of numerous well-arranged nanoleaves, which are approximately 20–30 nm in thickness and 100–200 nm in width. The grass-like nanostructure with many thin leaves can play an important role in increasing the sensing performance of as-derived samples because of its large specific surface area originating from the fine structure and more available active surface absorption sites [25]. When further increasing the amount of $Cu(NO_3)_2$ to 0.48 g, as-prepared samples exhibited aggregate morphology, and almost no fine-structures and uniformity could be observed in Fig. 1c and f, which indicates that a high level of precursors was detrimental to fine CuO nanostructures in our experiment.

Fig. 2 shows the XRD patterns of as-prepared samples using different amounts of $Cu(NO_3)_2$, which is used to identify the crystalline phase of different CuO nanostructures. All diffraction