



# Non-enzymatic electrochemical CuO nanoflowers sensor for hydrogen peroxide detection

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## ABSTRACT

The electrocatalytic activity of a CuO flower-like nanostructured electrode was investigated in terms of its application to enzyme-less amperometric H<sub>2</sub>O<sub>2</sub> sensors. The CuO nanoflowers film was directly formed by chemical oxidation of copper foil under hydrothermal condition and then used as active electrode material of non-enzymatic electrochemical sensors for H<sub>2</sub>O<sub>2</sub> detection under alkaline conditions. The sensitivity of the sensor with CuO nanoflowers electrode was 88.4 μA/mM cm<sup>2</sup> with a linear response in the range from 4.25 × 10<sup>-5</sup> to 4 × 10<sup>-2</sup> M and a detection limit of 0.167 μM (S/N = 3). Excellent electrocatalytic activity, large surface-to-volume ratio and efficient electron transport property of CuO nanoflowers electrode have enabled stable and highly sensitive performance for the non-enzymatic H<sub>2</sub>O<sub>2</sub> sensor.

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## 1. Introduction

Rapid and accurate determination of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is of practical importance in various fields such as food, clinical and environmental analyses. To date, H<sub>2</sub>O<sub>2</sub> detection has been mainly studied using spectrometry [1], fluorescence [2], chemiluminescence [3,4] and electrochemistry [5,6]. In particular, the electrochemical technique using an electrode modified with the redox active enzyme, horseradish peroxidase (HRP), has been extensively applied due to its simple, accurate, and fast analytical process [7,8]. The sensitivity of these sensors depends on the activity of the immobilized enzymes. However, one common drawback of enzyme-based sensors is insufficient stability originating from the nature of the enzymes, because enzymes are easy to deform thermally and chemically during fabrication, storage or use. In addition, the responses of most enzyme-based electrodes are not completely free from oxygen effects because the electron-mediating sites compete with oxygen dissolved in the solution [9].

Recently, it is of great interest to develop an enzyme-less electrochemical sensor with high sensitivity, fast response time, and long-term stability. In particular, electrochemically active nanomaterials consisting of metals [10–12], metallic carbon nanotubes [13–15], transition metal oxides [16,17], or conducting polymers [18,19] have been extensively studied for non-enzymatic electrochemical sensors, because they have large surface-to-volume ratio and increased catalytic activities.

Of these, CuO nanomaterials are one of the promising candidates for the active electrode material of non-enzymatic electrochemical sensors. Semiconducting CuO is a *p*-type semiconductor having a band gap of 1.2 eV and has shown its potential for applications in various fields, such as superconductors, magnetic storage media, solar energy transformation, electronics, batteries, sensors and catalysis [20,21]. Different synthetic methods have been developed for the fabrication of CuO nanostructures with various morphologies, including nanowire and nanosheet [22–24].

Although most of metallic Cu(0) nanomaterials are not stable enough to be used for electroanalysis because they are easily oxidized in air or aqueous solution, chemically more stable CuO nanomaterials have been studied for various applications including electrochemical H<sub>2</sub>O<sub>2</sub> sensors [17,25].

For example, electrochemical H<sub>2</sub>O<sub>2</sub> sensor based on Nafion and CuO nanoparticle modified Pt electrode was reported [17]. As another example, Jia et al. demonstrated the simple and convenient detection of H<sub>2</sub>O<sub>2</sub> using vertically aligned CuO nanowires [25]. The nanowires-modified electrode has benefit for increase

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of sensor performance. However efficient use of the high surface area of the structure may be limited by undesirable effects including the internal electrical resistance due to high aspect ratio of the semiconductor nanowires. The electrochemical properties of CuO nanomaterials are strongly dependent on its structural features such as crystal sizes, orientations, stacking manners, aspect ratios, and crystalline densities, which promote the study in this paper.

Herein, we describe a facile approach for developing an enzyme-less  $\text{H}_2\text{O}_2$  sensor based on CuO nanoflowers. The electrochemically active CuO nanostructure was grown from the substrate in a single step, and they can be directly used as sensor electrodes without additional processes such as surface modification or immobilization of expensive enzymes. Moreover, we achieve extremely large surface-to-volume ratio and efficient electron transport property due to the high-density single crystalline nano-petals in the electrode.

## 2. Experimental

### 2.1. Chemicals

$(\text{NH}_4)_2\text{S}_2\text{O}_8$  and  $\text{H}_2\text{O}_2$  were purchased from Sigma Chemical (St. Louis, USA). High-purity copper foils (Cu, 99.99%) were obtained from Nilaco Co. (Tokyo, Japan). Sodium hydroxide (NaOH) and potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ) were obtained from Duksan Pure Chemicals (Gyeonggi-do, Korea). All reagents were of analytical grade, and doubly distilled water was used throughout the experiments.

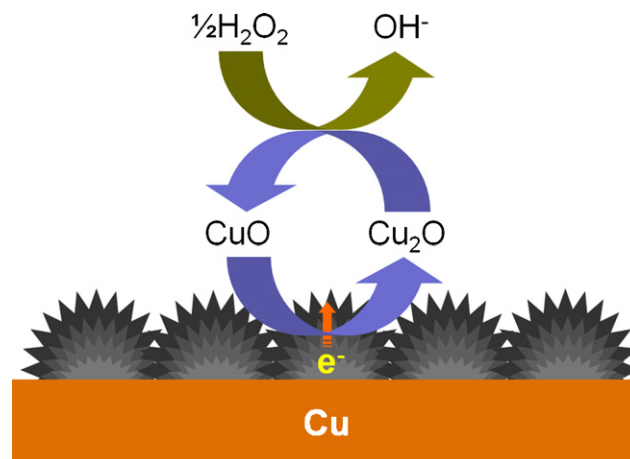
### 2.2. Preparation and characterization of CuO nanoflower and CuO nanowire electrodes

CuO nanoflowers were grown on a copper foil by a simple solution-based method [21]. Briefly, a piece of copper foil (5 mm × 5 mm × 0.2 mm) was immersed in 5 ml of 10 M NaOH solution and 13 ml of  $\text{H}_2\text{O}$  in a Teflon-lined stainless steel autoclave and then 2 ml of 1 M  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  solution was added. The autoclave was sealed and maintained at 100 °C for 12 h and was then cooled in tap water. The product was obtained in the form of a black thin film covering the copper foil. The product was washed with distilled water and ethanol, and then dried in air. As a comparative electrode, nanostructured electrode decorated with highly dense CuO nanowires was also prepared by previously reported method [26]. In short, a piece of copper foil was cleaned in 1.0 M HCl solution and distilled water. After drying it under  $\text{N}_2$  gas flow, it was treated in air for 4 h at 500 °C using a muffle furnace.

The morphologies and structures of the nanostructures were determined using transmission electron microscopy (TEM), high-resolution TEM (HR-TEM) equipped with selected area electron diffraction (SAED) and field emission scanning electron microscopy (FE-SEM). The images were taken with a JEM 2100F TEM (JEOL Ltd., Japan) operating at an accelerating voltage of 200 kV and a JSM 7000F SEM (JEOL Ltd., Japan). The samples for HR-TEM were prepared by placing a drop of precipitate on a carbon-coated copper grid and allowing it to dry in air. The phase purity of the CuO nanoflowers on the Cu substrates was characterized by powder X-ray diffraction (XRD) using a D8 DISCOVER powder X-ray diffractometer (Bruker AXS, USA) with Cu  $\text{K}\alpha$  radiation.

### 2.3. Electrochemical measurement

The electrochemical measurements were performed on a micro Autolab III potentiostat (Eco Chemie, Netherlands). A series of electrochemical experiments was conducted using a standard cell with three electrodes: a modified Cu electrode as the working electrode,

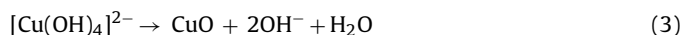
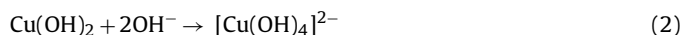
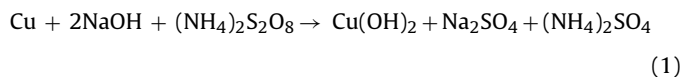


**Fig. 1.** A schematic view of the electrocatalytic mechanism of CuO nanoflowers for the reduction of  $\text{H}_2\text{O}_2$ .

a Pt counter electrode, and a saturated calomel electrode (SCE) used as a reference electrode. A 0.1 M NaOH solution was used as the supporting electrolyte because  $\text{H}_2\text{O}_2$  is reduced in an alkaline medium. The active surface area was estimated by cyclic voltammetry in 3 M KCl solution harboring 10 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  at a variety of scan rates. The applied potential ranged from  $-0.4$  to  $0.2$  V versus SCE with a Pt counter electrode.

### 2.4. Mechanisms for the formation of CuO nanoflowers and electron transfer in the modified electrode

The formation mechanism of the CuO nanoflowers film is as follows [23]:



When metallic Cu foils were immersed in a basic solution with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  oxidants, the foil surface quickly turned blue. Cu tends to dissolve in solutions that produce Cu complexes [27].

As shown in Eq. (3),  $[\text{Cu}(\text{OH})_4]^{2-}$  anions are produced as a precursor entity for the formation of CuO in a NaOH aqueous solution with a high concentration. Then, CuO is formed along with two hydroxyl ions and one water molecule. These CuO nuclei coalesce in order to decrease the total surface energy of the system and grow larger to form many CuO nanosheets with flower-like structures [24,27].

The electron-transfer mechanism in the modified electrode is shown in Fig. 1. In the catalytic mechanism for the reduction of  $\text{H}_2\text{O}_2$ , Cu(II) is reduced electrochemically to Cu(I), and  $\text{H}_2\text{O}_2$  is simultaneously reverted to  $\text{OH}^-$  along with the regeneration of the catalyst [17].

## 3. Results and discussion

### 3.1. CuO nanoflowers film

CuO nanoflowers film was directly fabricated by the oxidation reaction of copper foil under hydrothermal conditions [21]. As shown in Fig. 2, a nanostructured film with high density, flower-shaped CuO nanocrystals were produced on the copper foil. The CuO flowers consist of many thin CuO single crystalline petals with

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