A novel electrochemical sensor based on the copper-doped copper oxide nano-particles for the analysis of hydrogen peroxide

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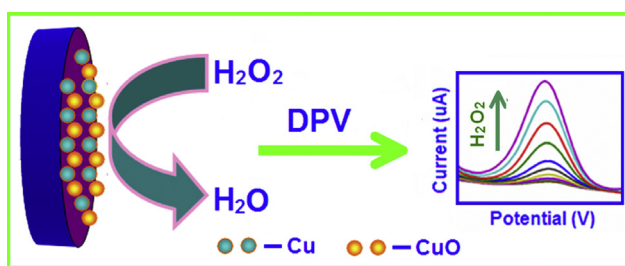[a] State Key Laboratory of Food Science and Technology, Nanchang University, Nanchang 330047, China
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HIGHLIGHTS

- A electrochemical sensor based on nano-particles, Cu@CuO/GCE, was constructed.
- The catalytic performance of the sensor was studied with the use of DPV technique.
- This sensor showed good electrocatalytic activity for the analysis of H_2O_2.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

A novel electrochemical sensor was constructed by depositing copper/copper oxide nano-particles on a glassy carbon electrode (GCE) to produce a Cu@CuO/GCE. The morphology and composition of this modified electrode were characterized with the use of scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD) techniques. The electrochemical properties of the novel modified GCE electrode were studied using various electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The catalytic performance of the sensor was studied with the use of differential pulse voltammetry (DPV) under optimized conditions. The constructed Cu@CuO/GCE sensor showed significantly better electrocatalytic activity for the analysis of the H_2O_2 in comparison to the Cu/GCE or GCE. The novel sensor produced a linear response for H_2O_2 analysis in the range of 0.005–8 mM and the detection limit was 0.23 μM (S/N = 3). Satisfactory results were obtained for H_2O_2 analyses of tap and lake waters. This performance compares very favorably with the results from several other commonly used techniques for analysis of H_2O_2.

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1. Introduction

It is well known that nano-particles have unique photonic, electronic, magnetic and catalytic attributes, and that their physical and chemical properties are related to their structures and morphologies [1]. Many different types of nano-particle have been synthesized in various ways, and in this context, many different metallic nanostructures have been reported. They have potential applications in electronics, catalysis and bioanalysis. In addition, the unique properties of nano-structural materials [2–9] could facilitate the discovery of new applications, which cannot be achieved with the use of bulk materials. One such area has involved the development of electrochemical sensors [10–12], especially those using inexpensive nano-particles, such as copper [13], nickel [14], and their oxides [15]. These substances

offer a range of morphologies, high specific surface area, good electrocatalytic activity, improved biocompatibility and electron transfer reactions at a lower overpotential.

Due to the potential application of nano-electronics, nano-wires of metallic and semiconductor materials have received considerable interest from both academic and industrial areas. For instance, copper oxide (CuO), a p-type semiconductor with a narrow band gap (1.2 eV), forms the basis of several high temperature superconductors, and has been used in the construction of solar cells, gas sensors and field transistors [16–21] because CuO has useful photoconducting and photochemical properties. Recently, CuO has been synthesized in its various morphologies and used in the construction of sensors. Also, the application of CuO, a useful catalyst, has been demonstrated by its replacement of the glucose oxidase in the procedure involving catalytic oxidation of glucose [22], alcohol [23], carbon monoxide at low-temperatures [24], and electrochemical catalysis of hydrogen peroxide [25,26].

In general, hydrogen peroxide (H_2O_2) is present in nature, particularly in waterways and various life systems. It is also used in different chemical processes involved with food, pharmaceutical, and environment, principally because it is a strong, non-polluting oxidant with water being its main reaction product. One of its common home and industrial uses is as a bleaching and cleaning agent, e.g. bleaching of textiles and paper as well as the degradation of organic pollutants [27]. Therefore, novel methods of analyses of H_2O_2 are important as they, potentially, will have many applications for the estimation of H_2O_2 in chemical, as well as bioscientific, industrial and home product samples.

Many kinds of chemically modified electrodes have been reported for the analysis of H_2O_2, and many of these are based on the immobilization of enzymes, such as horseradish peroxidase [28], cytochrome c [29] and myoglobin [30]. While these enzyme-based H_2O_2 methods have satisfactory selectivity and sensitivity, they are subject to environmental instability, complicated enzyme immobilization processes and are quite expensive [31,32]. On the other hand, inorganic metal oxides and their composites are effective, quite easy to prepare and are quite stable even at high temperatures [33]. In this context, by comparison, the Cu@CuO nano-particles are less expensive and easier to prepare relative to the noble metal modified electrodes. All this indicates that the Cu@CuO based sensor is potentially suitable for the analysis of hydrogen peroxide in many different applications.

The aims of this study were to: (1) research and develop a novel electrochemical sensor consisting of Cu@CuO/GCE; (2) investigate the electrochemical and electrocatalytic performance of the Cu@CuO/GCE, Cu/GCE and GCE, particularly for the analysis of H_2O_2, with the use of different techniques such as the scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD), as well as electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS); and (3) apply this sensor for the analysis of trace amounts of H_2O_2 in different types of water.

2. Materials and methods

2.1. Reagents

Copper chloride dihydrate ($CuCl_2·2H_2O$) was obtained from Shenyang Reagent Factory, Shenyang, China. Hydrogen peroxide solution (30 wt%) and other reagents were purchased from Shanghai Chemical Reagent Co., Shanghai, China. Unless otherwise stated, the chemicals in this work were all Analytical Grade reagents. They were used as received without further purification. A diluted H_2O_2 solution was freshly prepared before use. Sodium hydroxide solution (NaOH, 0.1 M) was prepared, and used as the supporting electrolyte. Double-distilled water was used throughout the experiments.

2.2. Instruments

The morphology and composition of the modified electrode were analyzed with the use of scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). This work was carried out on a JSM-6701F microscope system (JEOL Co., Tokyo, Japan). The operational power was 20.0 kV, and the magnification for all samples was 50,000×.

X-ray diffraction (XRD, Bede DI System, UK) was used to investigate the copper (II) oxide-doped copper (I) oxide nano-particles (Cu $K\alpha$ radiation (λ = 1.5406); Bragg angle range 10–80°).

All electrochemical experiments were performed on a CHI-660A electrochemical workstation (Shanghai Chenhua Apparatus Co., Shanghai, China) in conjunction with a standard three-electrode system: the working electrode – either the untreated or modified GCE (d = 3 mm); the counter electrode – a platinum wire, and the reference electrode – an Ag/AgCl (sat. NaCl). A cell stand (Model BAS C1A, USA) was used for voltammetric scanning and to stir the test solutions during an experiment.

The small GCEs were modified with different materials without any further coating because they were already electro-conducting.

EIS experiments for the modified GCE were also performed with the use of the CHI-660A electrochemical workstation, and 5×10^{-3} mol L^{-1} [Fe(CN)$_6$]$^{3-/4-}$ solution containing 0.1 mol L^{-1} KCl (1:1) was the experimental medium.

2.3. Preparation of the variously modified GCEs

The GCE was polished to a mirror-like shine with 0.1 and 0.05 μm alumina slurry sequentially, and then, the electrode was sonicated in nitric acid (1:1, v/v), ethanol and double-distilled water, in turn. The electro-deposition of the Cu@CuO nano-particles was performed on the surface of an untreated GCE. Thus, the GCE was dipped into a solution containing 10 mM $CuCl_2$ and 100 mM KCl, which had been pre-purged with pure nitrogen for 15 min. Then, the electro-deposition step was performed at a potential of −0.4 V for 60 s. The electrode was then rinsed several times with water and dried in air. Following this procedure, the modified electrode was scanned with the use of CV in 100 mM NaOH over the potential range of −0.5 to 0.3 V at 100 mV s^{-1} for 10 cycles. This allowed the Cu nano-particles to be oxidized to CuO nano-particles. Finally, the electrodes were rinsed with double-distilled water and dried in air [34].

3. Results and discussion

3.1. X-ray diffraction analysis of the Cu@CuO nano-particles on the modified GCE

In general, XRD is used to analyze the structural features of chemical compounds and nano-particles, and in this work, it was used for the analysis of the electrodeposited nano-particles on the GCE (Fig. 1). The obtained XRD diffractogram of the GCE surface had a single strong diffraction peak at 20° (2θ scale). This peak was related to the Cu phase. There was another weaker peak at 25°, which was also attributed to the Cu phase, as were three other weak diffractions at approximately 35, 51 and 60°. These corresponded to the diffraction peaks from the −1 1 1, −2 0 2, and −1 1 3 planes of CuO [35,36]. Thus, the XRD of the deposited nano-particles indicated that Cu and CuO nano-particles were present on the surface of the modified electrode.