Cuprous Oxide Cubebox for Nonenzymatic Amperometric Hydrogen Peroxide Detection

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Abstract. Cuprous oxide (Cu2O) nanomaterial has been successfully obtained by a simple sol-gel technique. The characterization indicated that the powders have a good crystalline structure, and the synthesis was successfully controlled in nanoscale. Cyclic voltammetry (CV) revealed that Cu2O cubebox exhibited a direct electrocatalytic activity for the reduction of hydrogen peroxide (H2O2) in sodium hydroxide solution. The enzyme-less amperometric sensor used in the detection of H2O2 with detection limit of 81.69μM (S/N = 3) over wide linear detection ranges up to 0.39 mM and with a high sensitivity of 444.7μA·mM−1·cm−2, and a possible mechanism was also given in the paper.

Introduction

Hydrogen peroxide detection is of critical in the fields of food, chemistry, clinical, biology, pharmaceutical and environmental analyses[1]. Currently, abundant number of methods can detect the level of H2O2, such as spectroscopic methodology and electrochemistry, and the electrochemical detection of H2O2 was considered as a lower detection limit and a low cost compared with the former. In a typical experiment, the electrochemical technique using an electrode modified with theredox active enzyme (e. g. horseradish peroxidase (HRP)), has beenextensively applied due to its simple, accurate, and fast analytical process. However, enzymes are very expensive and can only work effectively under proper conditions, and it is not conducive to a wide range of applications. In contrast, nonenzymatic biosensors were advocated, such as amperometric sensors, which is based on metal oxide[2].

Of these, Cu2O nanomaterials are one of the promising candidates for the active electrode material of non-enzymatic electrochemical sensors. Semiconducting Cu2O is a p-type semiconductor having a band gap of 2.7 eV and has shown its potential for applications in various fields, such as solar energy transformation, electronics, lithium ion batteries, catalysis and gas sensor[3]. And different synthetic methods have been developed for the fabrication of Cu2O nanostructures with various morphologies. However, the application in nonenzymatic hydrogen peroxidesensing of cuprous oxide has rarely been reported.

In this paper, we present a simple and effective method for the synthesis of cuprous oxide cubebox nanomaterial with crystalline wall. The sensor based on cuprous oxide cubebox showed good hydrogen peroxide sensing properties, and a possible mechanism was also given.

Experimental

References[4, 5] method, 10 mL of an aqueous solution of NaOH (2 M) was added dropwise into 100 mL deionized water of a mixture solution containing CuCl2·5H2O (0.15 g), and PVP (Mw = 55000, 0.50 g) dissolved completely under stirring. During the process, the solution color turned into light blue, and then dark green. After 0.5 h, 10 mL of an ascorbic acid solution (0.6 M) was added dropwise into the above solution, the procedure was heated in a water bath at 45°C for 3 h. The resulting precipitate was collected by centrifugation, followed by washing with distilled water and...
absolute ethanol to remove the residual inorganic ions and polymer, and finally dried in vacuum at 60°C, then brick red Cu₂O cubeboxes were synthesized.

**Characterization**

The powder XRD patterns were tested on a D8 Tools X-ray diffraction instrument using the CuKα radiation at 40 kV and 30 mA. The morphology of products was characterized by a Hitachi S-3000N scanning electron microscope (SEM).

**Fabrication of working electrodes and electrochemical experiments**

Cyclic voltammetric (CV) and amperometric (i–t) measurements were performed using CHI 660E Electrochemical Workstation (CH Instruments, USA). Ag/AgCl (3 M KCl) electrode and Pt wire were used as the reference electrode and the counter electrode, respectively. Bare glassy carbon electrode (GCE, dia. 3 mm) was polished with 1 μm and 0.05 μm alumina slurries, and then successively sonicated in ethanol, and deionized water followed by drying at room temperature. An appropriate volume of Cu₂O/ethanol suspension (5 mg/mL) was dropped on the surface of GCE. 5 mL of NaOH with an appropriate concentration was applied as the electrolyte in the study[6].

**Results and discussion**

![SEM image of Cu₂O powders, inset is the XRD image](image1)

The scanning electronmicroscopy (SEM) image in Figure 1 shows the brick red powders heated in a water bath at 45°C. It is clearly to see that the morphology of Cu₂O is mainly cubebox with uniform size at average about 900nm. Inset of Figure 1 is the XRD image, all diffraction peaks match well with the standard JointCommittee on Powder Diffraction Standards (JCPDS) card (05-0667). No other impurity peaks can be observed in this pattern. This demonstrates that the as-prepared brick powders are indeed Cu₂O.

![CVs of the Cu₂O/GCE composed of different scan numbers (1-10) in the presence of 0.1 mM H₂O₂ containing 0.1 M NaOH solution at a scan rate of 50 mV/s](image2)

Fig. 2. CVs of the Cu₂O/GCE composed of different scan numbers (1-10) in the presence of 0.1 mM H₂O₂ containing 0.1 M NaOH solution at a scan rate of 50 mV/s
The results characterized indicated that the synthesis was successfully controlled in nanoscale, and cuprous oxide has a good crystalline structure. The CVs of the electrochemical sensors which base on as-prepared Cu$_2$O was investigated in the presence of 0.1 mM H$_2$O$_2$ containing 0.1 M NaOH solution in the range from -0.6 V to 0.6 V vs. Ag/AgCl at a scan rate of 50 mV/s. The first cycle needs higher oxidation potential. In the next cycles, the anodic and cathodic peaks shift lower potentials in the first cycle. It is a progressive oxidation of the Cu$_2$O as the scan cycles increase. The oxidation rate of Cu$_2$O is slowed, and a pair of redox peaks tends to stabilize with anodic peak at about 0.4 V and cathodic peak at about 0.15 V in Fig. 2, the wide positive work potential window is favorable for the Cu$_2$O/GCE electro-oxidation of H$_2$O$_2$. Yielding an $\Delta E_p$ value of 0.25 V where the anodic potential is much greater than the cathodic potential, shows that the electrode surface occurs larger polarization.

![Fig. 3](image)

Fig. 3. (a) Amperometric responses in 0.1 M NaOH solution at 0.4 V of sequential additions of H$_2$O$_2$ at the Cu$_2$O/GCE electrode. (b) Calibration curve of the Cu$_2$O/GCE electrode at a working potential of 0.4 V, with $R^2=0.9983$.

A high sensitivity could be obtained by this method. The potential was selected as 0.4 V (vs Ag/AgCl). The amperometric response to H$_2$O$_2$ detection on Cu$_2$O/GCE electrode performed in 0.1 M NaOH solutions at room temperature is shown in Figure 3a. Upon sequential addition of H$_2$O$_2$, the electrochemical response was recorded as the solution was stirred constantly. Fig. 3a shows the amperometric responses at the applied potential of the Cu$_2$O/GCE electrodes with successive increments of the H$_2$O$_2$ concentration from 0 to 0.39 mM. All the results indicated that the Cu$_2$O/GCE sensor had a better sensitivity and a lower detection limit for H$_2$O$_2$. The corresponding calibration curve (Fig. 3b) is linear up to 0.39 mM with a sensitivity of 444.7 $\mu$A·mM$^{-1}$·cm$^{-2}$ and a detection limit of 81.69 $\mu$M (S/N = 3), but saturated at a higher H$_2$O$_2$ concentration.

Sensors modified with Cu$_2$O nanoparticles show good performances through increasing the surface area and enhancing the mass transport. Therefore, it is reasonable to expect that processing Cu$_2$O into nanostructured materials could enhance its performance in the catalytic activity towards the electro-oxidation of H$_2$O$_2$.

Conclusions

Cuprous oxide cubeboxes were successfully obtained through a simple and effective nanocasting method. The electrochemical sensor based on cuprous oxide cubeboxes exhibit good H$_2$O$_2$ sensing
properties with high sensitivity. And it could be seen as a promising candidate for detecting low concentration of H₂O₂ under non-harsh conditions.

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Reference