Cuprous Oxide Cubebox for Nonenzymatic Amperometric Hydrogen Peroxide Detection

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Abstract. Cuprous oxide (Cu_2O)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 Cu_2O cubebox exhibited a direct electrocatalytic activity for the reduction of hydrogen peroxide (H_2O_2) in sodium hydroxide solution. The enzyme-less amperometric sensor used in the detection of $H_2O_2$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 444.7$\mu A \cdot mM^{-1} \cdot cm^{-2}$, 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 H_2O_2, such asspectroscopic methodologyand electrochemistry, and the electrochemical detection of H_2O_2 was considered as a lower detection limit and a low cost compared with the formor. In a typical experiment, theelectrochemical technique using an electrode modified withtheredox active enzyme (e. g. horseradish peroxidase (HRP)), has beenextensively applied due to its simple, accurate, and fast analyticalprocess. 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, Cu_2O nanomaterials are one of the promising candidates for the active electrode material of non-enzymatic electrochemical sensors. Semiconducting Cu_2O 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 Cu_2O 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 oxidecubebox nanomaterial with crystalline wall. The sensor based on cuprous oxidecubebox 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 addeddropwise into 100 mL deionized water of a mixture solution containing $CuCl_2 \cdot 5H_2O$(0.15 g), and PVP (Mw = 55000, 0.50 g) dissolved completelyunder stirring.During the process, thesolution color turned into light blue, and then dark green. After 0.5 h, 10 mL of an ascorbic acid solution (0.6 M) wasadded dropwise into the above solution,the procedure was heated in a water bath at 45°C for 3 h. The resulting precipitate wascollected by centrifugation, followed by washing with distilledwater and

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absolute ethanol to remove the residualinorganic ions and polymer, and finally dried in vacuum at 60°C, then brick redCu_2O 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 Cu_2O/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

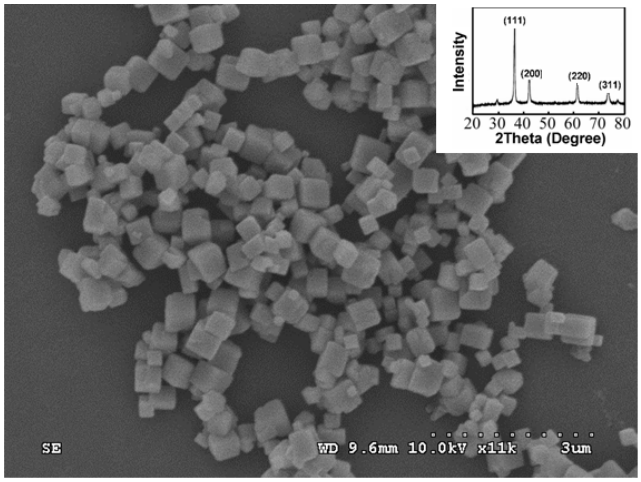

Fig.1. SEM image of Cu_2O powders, inset is the XRD image

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 Cu_2O 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 otherimpurity peaks can be observed in this pattern. This demonstratesthat the as-prepared brick powders are indeed Cu_2O.

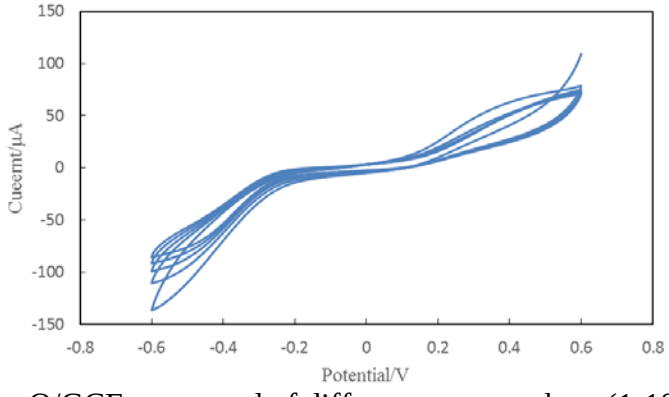

Fig. 2. CVs of the Cu_2O/GCE composed of different scan numbers (1-10) in the presence of 0.1 mMH_2O_2containing 0.1 M NaOH solution at a scan rate of 50 mV/s

The results characterized indicated that the synthesis was successfully controlled in nanoscale, and cuprous oxide has a good crystalline structure. The CVs of theelectrochemical sensors which base on as-prepared $Cu_2O$was investigated in the presence of 0.1 mM H_2O_2 containing0.1 M NaOH solution in the range from -0.6V to 0.6 V vs. Ag/AgClat a scan rate of 50 mV/s. The first cycle needs higher oxidation potential. In the next cycles, the anodic and cathodic peaks shiftto lower potentials in the firstcycle. It is a progressive oxidation of theCu_2O as the scan cycles increase.The oxidation rate of $Cu_2O$is slowed, and a pair of redox peak tends to stabilize with anodic peak at about 0.4 V andcathodic peak at about 0.15 V in Fig.2, the wide positive work potentialwindow of is favorable for the Cu_2O/GCEelectro-oxidation of H_2O_2. Yielding an ΔE_pvalue of0.25Vwhere the anodic potential is much greater thanthe cathodic potential,shows that the electrode surface occurs larger polarization.

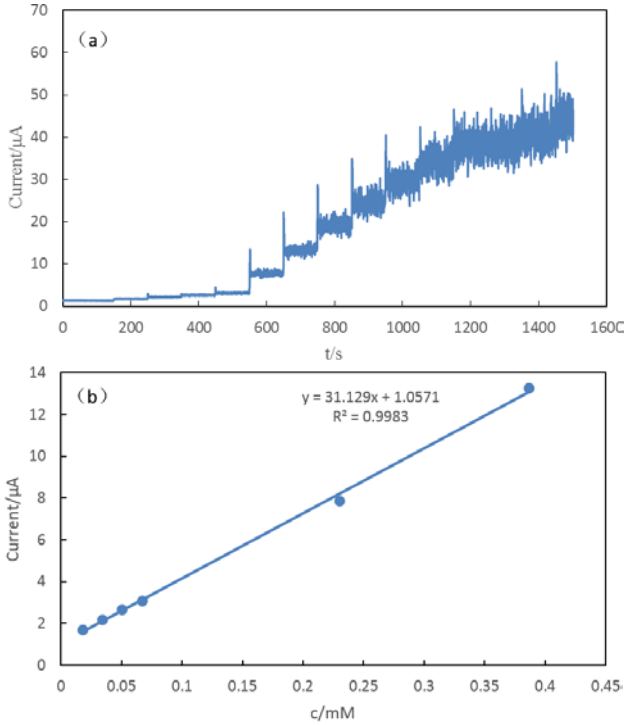

Fig. 3.(a) Amperometric responses in 0.1 M NaOH solution at 0.4 V of sequential additions of H_2O_2 at the Cu_2O/GCE electrode.(b) Calibration curve of the Cu_2O/GCE electrode at a working potential of 0.4 V, with R^2=0.9983.

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_2O_2 detection on Cu_2O/GCE electrode performed in 0.1 M NaOH solutions at room temperature is shown in Figure 3a.Upon sequential addition of H_2O_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_2O/GCE electrodes with successive increments of the H_2O_2 concentration from 0 to 0.39mM. All the results indicated that the Cu_2O/GCE sensor had a better sensitivity and a lower detection limit for H_2O_2. The corresponding calibration curve (Fig. 3b) is linear up to 0.39mM with a sensitivity of 444.7μA·mM^{-1}·cm^{-2} and a detection limit of 81.69μM (S/N = 3), but saturated at a higher H_2O_2 concentration.

Sensors modified with Cu_2O nanoparticles show good performances through increasing the surface area and enhancing the mass transport. Therefore, it is reasonable to expect that processing Cu_2O into nanostructured materials could enhance its performance in the catalytic activity towards the electro-oxidation of H_2O_2.

Conclusions

Cuprous oxide cubeboxeswere successfully obtained through a simple and effective nanocasting method. The electrochemicalsensor based on cuprous oxidecubeboxes exhibit good H_2O_2sensing

properties with high sensitivity. And it could be seen as a promising candidate for detecting low concentration of H_2O_2 under non-harsh conditions.

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Reference

[1] Zhang L, Li H, Ni Y, Li J, Liao K, Zhao G. Porous cuprous oxide microcubes for non-enzymatic amperometric hydrogen peroxide and glucose sensing. *Electrochemistry Communications*. 2009;11:812-5.

[2] Song MJ, Hwang SW, Whang D. Non-enzymatic electrochemical CuO nanoflowers sensor for hydrogen peroxide detection. *Talanta*. 2010;80:1648-52.

[3] Geng B, Liu J, Zhao Y, Wang C. A room-temperature chemical route to homogeneous core–shell Cu_2O structures and their application in biosensors. *CrystEngComm*. 2011;13:697.

[4] Sui Y, Fu W, Yang H, Zeng Y, Zhang Y, Zhao Q, et al. Low Temperature Synthesis of Cu_2O Crystals: Shape Evolution and Growth Mechanism. *Crystal Growth & Design*. 2009;10:99-108.

[5] Wang D, Mo M, Yu D, Xu L, Li F, Qian Y. Large-Scale Growth and Shape Evolution of Cu_2O Cubes. *Crystal Growth & Design*. 2003;3:717-20.

[6] Zhang Y, Su L, Manuzzi D, de los Monteros HV, Jia W, Huo D, et al. Ultrasensitive and selective non-enzymatic glucose detection using copper nanowires. *Biosensors & bioelectronics*. 2012;31:426-32.