Hydrogen peroxide sensing using Cu_2O nanocubes decorated by Ag-Au alloy nanoparticles

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ABSTRACT

To develop the high efficiency nonenzymatic hydrogen peroxide (H_2O_2) sensor, Cu_2O nanocubes decorated by Ag-Au alloy nanoparticles (Ag-Au/Cu_2O nanocomposites) were designed and synthesized in this paper. By studying for the electrocatalytic activities toward H_2O_2 reduction, the as-prepared Ag-Au/Cu_2O nanocomposites exhibited higher performance toward electrochemical oxidation of H_2O_2 in 0.2 M phosphate buffered saline (PBS) solution than pristine Cu_2O nanocubes, Ag-Cu_2O and Au-Cu_2O nanocomposites, and the detection limit was 1.30 μM and the sensitivity was 4.16 μA cm^{-2} mM^{-1}, respectively. The enhanced electrochemical activity of Ag-Au/Cu_2O nanocomposites indicated that the Ag-Au alloys dispersed on the surface of Cu_2O played a key role in the sensing properties enhancement, and the possible mechanisms for the enhanced electrochemical activity of Ag-Au/Cu_2O nanocomposites have been detailed discussed. In addition, the anti-interference capability experiment indicated that the Ag-Au/Cu_2O nanocomposites have good selectivity toward H_2O_2. The excellent performance demonstrated the potential application of the Ag-Au/Cu_2O nanocomposites for H_2O_2 detection.

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1. Introduction

Study on the rapid, accurate, reliable detection of H_2O_2 has been received great attention in recent, since H_2O_2 is a common oxidizing agent and an essential intermediate in the field of biomedical, pharmaceutical, industrial, environmental protection and electrochemistry [1–4]. Many analytical techniques, including chemiluminescence, titrimetry spectrophotometry, fluorescence and electrochemical method have been developed to detect H_2O_2 [5–11]. Among these methods, non-enzymatic electrochemical sensors are of particular interest for their low-cost, stability and suitability for real-time detection [12–15]. Nanomaterials, including metal nanoparticles, metal alloys, transition metal oxide, and carbon based nanomaterials have been intensively employed to construct electrochemical H_2O_2 sensors [16–20]. However, using the materials above-mentioned in the electrochemical sensors to promote the redox reaction processes and electrochemical detection H_2O_2 are still in the early stage. Therefore, it is greatly desirable to explore novel nanomaterial sensors for the fast and accurate detection of H_2O_2.

As a typical transition metal oxide, cuprous oxide (Cu_2O) has attracted increasing attention as promising candidate for electrochemical sensors due to their low cost and significant catalytic activities [21,22]. Unfortunately, pristine Cu_2O sensors displayed low sensitivity and narrow linear detection ranges. Combination with other materials (such as graphene and metal particles) is one of the most effective ways to improve the performance of metal oxide-based and carbon-based sensors [23–25]. Among these promising materials, noble metal nanoparticles (such as Ag, Au, Pt, etc.) could largely enhanced the electrocatalytic activity toward H_2O_2 reduction, due to their good stability, high electrocatalytic activity, and the ability to enhance the electrode conductivity and facilitate the electron transfer [26–28]. Notably, bimetallic alloys have recently been extensively explored for their promising applications such as catalysis and sensors because of the existence of interaction between two components in bimetallic alloys [29,30]. They often present many favorable properties in comparison with the corresponding monometallic counterparts, which include high catalytic activity, catalytic selectivity and better resistance to deactivation [31]. Among these alloys, Ag-Au bimetallic nanomaterials attracted great attention because of some unique

properties of Ag and Au, such as perfect electro conductibility, biocompatibility and high catalytic activities [32]. However, in the case of Ag-Au bimetallic nanoparticles, no study is focused on its excellent ability to enhance the H_2O_2 electrochemical sensor efficiency of non-enzymatic electrochemical sensors, especially Cu_2O nanomaterials.

In this work, Cu_2O nanocubes decorated by Ag-Au alloy nanoparticles (Ag-Au/Cu_2O nanocomposites) have been successfully synthesized by a multi-step method. The electrochemical measurements were applied to elucidate the sensing application of Ag-Au/Cu_2O nanocomposites. Compared with pristine Cu_2O nanocubes, Ag-Cu_2O and Au-Cu_2O nanocomposites, the as-prepared Ag-Au/Cu_2O nanocomposites exhibited enhanced H_2O_2 electrochemical sensor efficiency. Furthermore, the Ag-Au/Cu_2O nanocomposites exhibited good selectivity toward H_2O_2 by using AA, Glu and UA as the interfering species. Thus, we believe that the Ag-Au/Cu_2O nanocomposites with excellent performance could be used as a promising sensor for H_2O_2 detection.

2. Experimental section

2.1. Materials

Ascorbic acid (AA), uric acid (UA), glucose (Glu), hydrogen peroxide (H_2O_2, 30 wt%), ethanol, sodium hydroxide, copper acetate monohydrate, silver nitrate and gold potassium chloride were purchased from Sinopharm Chem. Reagent Co., Ltd (Shanghai, China). All chemicals were of analytical degree and used as received without further purification.

2.2. Synthesis of the Cu_2O nanocubes

Cu_2O nanocubes were synthesized using the method reported previously [33]. In a typical synthesis method, a mixture including 20 mL of 0.009 M AA solution and 32 mL of 0.391 M NaOH solution was added into 32 mL of as-prepared 0.005 M Cu(Ac)$_2$·H_2O solution under stirring and stirred vigorously for 30 min. During this time, the solution turned to yellow and turbid, indicating that the Cu_2O was formed. Then, the obtained precipitates were collected, washed with distilled water and absolute ethanol several times alternately, and dried in vacuum at 60 °C for 5 h. In addition, the sample was dispersed in ethanol for further characterization. All the experiments were carried out at room temperature.

2.3. Synthesis of Ag(Au)/Cu_2O and Ag-Au/Cu_2O nanocomposites

Ag/Cu_2O nanocomposites were synthesized based on a previous method [34]: 0.02 g of as-prepared Cu_2O nanocubes were dispersed into 50 mL of 30 °C pre-heated distilled water by sonication, and then the suspension was irradiated by an iodine tungsten (500 W). Under continuous magnetic stirring, 1 mL of AgNO$_3$ solution (0.035 M) was injected into the above suspension, and the suspension was further irradiated for 20 min. The resulting products were collected by centrifugation, washed with distilled water and absolute ethanol several times alternately, and dried under vacuum at 50 °C for 2 h.

The synthesis method for the Au/Cu_2O nanocomposites was similar to the procedure of Ag/Cu_2O nanocomposites, except that 1 mL of 0.016 M KAuCl$_4$ solution was used instead of 1 mL of 0.035 M AgNO$_3$ solution.

The Ag-Au/Cu_2O nanocomposites were synthesized by a two-step method on the basis of above-mentioned procedure. First, Au/Cu_2O nanocomposites were prepared according to the above method. Then, the as-synthesized Au/Cu_2O nanocomposites were used to fabricate Ag-Au/Cu_2O nanocomposites instead of pure Cu_2O nanocubes in the procedure for the synthesis of Ag/Cu_2O nanocomposites.

2.4. Preparation of the modified electrode and electrochemical measurements

1 mg of Ag-Au/Cu_2O nanocomposites and 10 μL of Nafion solution (5 wt%) were dispersed in 1 mL of water-isopropanol mixed solvent (v/v = 3:1) by at least sonication for 30 min to form a homogeneous catalyst solution. The glassy carbon electrode (GCE) was polished in 0.3 and 0.05 nm alumina slurry, respectively, and washed with ultrapure water followed by sonication in water for 10 min. Then 10 μL of the mixture solution was dropped onto the surface of the cleaned GCE and left to dry at ambient temperature to obtain Ag-Au/Cu_2O nanocomposites modified electrode, referred as Ag-Au/Cu_2O/GCE. Amperometric and cyclic voltammetry (CV) experiments were carried out by a CHI 650D electrochemical analyzer (CH Instruments, Inc., Shanghai), in a home-made three electrode electrochemical cell consisting of a twisted platinum wire as an auxiliary electrode, a saturated calomel electrode (SCE) as a reference electrode and a modified-GCE (0.2 cm^2) as a working electrode. All experiments were carried out at the room temperature. Prior to the experiment, the electrolyte consisting of a solution of 0.2 M phosphate buffer solution (PBS, pH 7.4), was purged with high-purity nitrogen for at least 30 min and a nitrogen atmosphere was maintained over the solution. The electrochemical sensor activities test of Cu_2O nanocubes, Ag/Cu_2O and Au/Cu_2O nanocomposites were used the similar method as above, and the modified electrodes were denoted as Cu_2O/GCE, Ag/Cu_2O/GCE and Au/Cu_2O/GCE, respectively. Furthermore, the amperometric response for AA, UA and Glu were also same as the above method.

2.5. Characterization

Purity and crystallization of the samples were characterized by powder X-ray diffraction on a D8 Advance X-ray spectrometer (Bruker, Germany) at 40 kV and 200 mA with monochromatic Cu Ka (λ = 1.5418 Å) radiation. Transmission electron microscopy and high resolution transmission electron microscopy (TEM and HRTEM) images and energy dispersive spectrometer (EDS) mapping were taken on a Tecnai G2 F30 S-TWIN TEM instrument (FEI, America) with an accelerating voltage of 300 kV. Scanning electron micrograph (SEM) and energy dispersive spectrometer (EDS) were taken on a field emission SEM (FESEM) instrument (Hitachi S-4800, Japan). The surface areas of the sample was measured by a TriStar II 3020-BET/BJH Surface Area (Micromeritics Instrument Corporation, America). X-ray photoelectron spectroscopy (XPS) was performed on an ADES 400 (VG, England) instrument with Mg K-ADES source. Electrochemical measurements were performed with a CHI 650D electrochemical analyzer (CH Instruments, Inc., Shanghai).

3. Results and discussion

The morphology and structure details of Ag-Au/Cu_2O nanocomposites were investigated by SEM and TEM observations. As shown in Fig. 1a, SEM image confirms the well-dispersed and well-shaped nanocube structure of pristine Cu_2O with an average size of 300 nm, and the surface of the Cu_2O nanocubes are smooth. Fig. 1b exhibits a typical SEM image of Ag-Au/Cu_2O nanocomposites, which indicates that there are lots of small nanoparticles with a small size supported on the nanocube, and the whole size of the Ag-Au/Cu_2O nanocomposite changed a little larger than the pristine Cu_2O nanocube. Both of the TEM images of pristine Cu_2O nanocubes and Ag-Au/Cu_2O nanocomposites (Fig. 1c and d) further confirm the morphological analysis of SEM images. The shape and