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Pyrocatechol violet-assisted in situ growth of copper nanoparticles on carbon nanotubes: The synergic effect for electrochemical sensing of hydrogen peroxide

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ABSTRACT

Copper nanoparticles (CuNPs) form by in situ electrochemical reduction of chelated copper ions on the electrode with pyrocatechol violet (PCV) and single walled carbon nanotubes (SWCNTs). The electrodeposited PCV is used as chelating agent for copper ions as well as the redox mediator during the electrocatalysis of H_2O_2. Due to the synergic effect of SWCNTs/PCV/CuNPs, the modified electrode gives enhanced analytical performance for detection of H_2O_2 at -0.2 V vs. SCE with an enlarged linear response as a function of peroxide concentration spanning 2×10^{-6} to 1.2×10^{-2} M.

1. Introduction

Fast and easy determination of H_2O_2 has attracted much attention due to its important role in pharmaceutical, clinical, environmental, mining, textile and food manufacturing applications [1]. Several methods such as titrimetry [2], spectrophotometry [3], chromatography [4], chemiluminescence [5], and colorimetry [6] are available for determination of H_2O_2.

Electrochemical sensors and biosensors have become an important tool for detection of chemical and biological components, because they have exceptional performance and capabilities, which include high specificity and sensitivity, rapid response, low cost, relatively compact size and user-friendly operation [7]. Enzymatic electrochemical sensors based on immobilization of enzymes such as myoglobin [8], horseradish peroxidase [9] and hemoglobin [10] are used for selective and sensitive analysis of H_2O_2. Nevertheless, the activity of biomolecules is susceptible to environmental temperature, pH value, humidity, and toxic chemicals. Also, both high cost and the complicated procedure for immobilizing enzymes on the electrode are obstacles for its application. Thus, direct determination of H_2O_2 at enzyme free sensors is of great significance.

Copper based materials, such as copper bulk metal, copper nanoparticles (CuNPs) and copper complexes, have attracted considerable interest as sensors and biosensors due to their low cost, plenty of morphologies, high specific surface area, good electrocatalytic activity, and the possibility of promoting electron transfer reactions at a lower overpotential [11]. CuNPs have shown very satisfactory catalytic activity toward glucose oxidation or H_2O_2 reduction and have been used in the development of glucose/H_2O_2 sensors by adopting different schemes for their integration with the transducer surface [12–18]. In this present work, a novel sensing system was developed based on CuNPs, pyrocatechol violet (PCV) and single walled carbon nanotubes (SWCNTs).

Pyrocatechol violet (PCV, with the chemical structure shown in Scheme 1) is a sulfone phthalein dye prepared from condensing two moles of pyrocatechol with one mole of *o*-sulphobenzoic acid anhydride. It has been demonstrated that materials from catechol and gallate families, containing —OH groups bonded to the adjacent carbon atoms of the aromatic ring, strongly adsorbed on various inorganic materials. It is important to note that such bonds improved charge transfer between inorganic and organic materials [19]. After electrodeposition, PCV film possesses the larger real surface area, π–π conjugated bond, a great deal of active sites and better conductivity [20,21]. Since the special sidewall curvature and π-conjugative structure of SWCNTs [22] facilitated its interaction with PCV during the electrochemical deposition of the latter, the electron transfer rate and conductivity can be efficiently enhanced by introduction of SWCNTs. PCV as a chelating agent has been widely used because of its high complex formation

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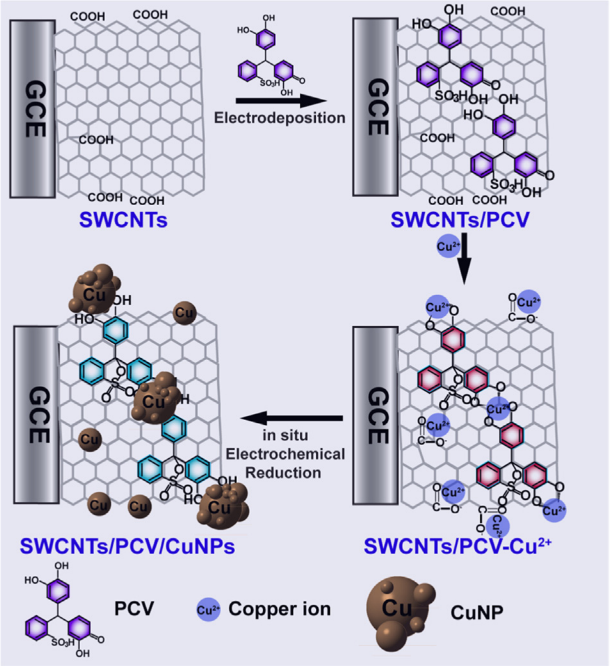

Scheme 1. Schematic illustration of stepwise preparation of SWCNTs/PCV/CuNPs-modified GCE.

constants with metal ions for spectrophotometric metal determinations [23,24] and for preconcentration of trace metal ions from aqueous solutions [25]. Herein, we presumed that the electrodeposited PCV can work as chelating agent for copper ions, CuNPs can be obtained by in situ electrochemical reduction of the preconcentrated copper ions on the chelating electrode, and the enhanced H_2O_2 catalysis can be realized due to the cooperation of the electrodeposited PCV and CuNPs.

2. Experimental

2.1. Materials

Pyrocatechol violet (PCV) was obtained from Sangon Chemicals (China). Single-walled carbon nanotubes with carboxylic acid groups (SWCNTs, 4–5 nm outer diameters, 0.5–1.5 μm length and >90% purity) were obtained from Sigma–Aldrich (USA). H_2O_2 solution (30 wt%) was purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). The molar concentration of H_2O_2 solution (30 wt%) is about 9.8 M. Thus, 1 M H_2O_2 solution was prepared by dissolving 0.102 mL H_2O_2 solution (30 wt%) in 0.898 mL water. The solution was kept at 4 °C and in dark. All other chemical reagents were of analytical grade and used as received without further purification. Double-distilled water was used for preparing aqueous solutions. Phosphate buffer solutions (PBS) were prepared with 0.1 M K_2HPO_4 and KH_2PO_4 using 0.1 M KCl.

2.2. Apparatus

A CHI 660 electrochemical workstation (CHI Co., USA) was used for was used for cyclic voltammetry (CV), differential pulse voltammetry (DPV) and amperometric measurements. All electrochemical studies were performed with a conventional three electrode system. A saturated calomel electrode (SCE) and a Pt wire electrode were used as reference and counter electrodes, respectively. All the potentials mentioned below are relative to SCE. The working electrode was a glassy carbon electrode (GCE) (diameter 3 mm). The atomic force microscope (AFM) images were performed with 5500 AFM/SPM (Agilent, USA). The X-ray photoelectron spectroscopy (XPS) experiments were carried out on K-Alpha (Thermo Fisher Scientific Co., USA). The Gaussian-Lorentzian distribution was used for fitting the spectra for each peak, in order to determine the binding energy of the core levels of the different elements.

2.3. Preparation of the modified electrode

A glassy carbon electrode (GCE) was polished carefully with 0.05 μm alumina particles on silk followed by sonication in deionized water followed by ethanol and dried in air prior to use. GCE/SWCNTs, GCE/SWCNTs/PCV and GCE/SWCNTs/PCV/CuNPs were prepared following the protocol illustrated in Scheme 1. Initially, SWCNTs were dispersed in dimethyl formamide (DMF) under sonication leading to a concentration of 0.2 mg ml^{-1}. The modification of GCE with SWCNTs was performed by casting 3 μl of SWCNTs/DMF suspension on the electrode surface and dried in air. This obtained electrode was denoted as GCE/SWCNTs. The electrochemical deposition of PCV was performed over the surface of GCE/SWCNTs, in a 0.1 M PBS (pH 7) containing 1 mM PCV and 0.1 M KCl, through cyclic voltammetry between −0.2 to 0.5 V for 20 cycles at a scan rate of 20 mV s^{-1}. The modified electrode obtained above were denoted as GCE/SWCNTs/PCV and rinsed carefully with doubly distilled water before further modification. The coordination of copper ions with SWCNTs/PCV modified electrode was carried out by immersing GCE/SWCNTs/PCV for 30 min in sodium acetate/acetic acid buffer solution (pH 6.0) containing 0.01 M copper nitrate. After accumulation of the metal ion, the electrode was carefully washed with distilled water under stirring conditions. The potentiostatic deposition of copper was carried out by immersing the Cu^{2+}-chelated electrode (GCE/SWCNTs/PCV-Cu^{2+}) in 0.5 M NaCl aqueous solution at −0.9 V vs. SCE for 30 s. The resultant electrode was denoted as GCE/SWCNTs/PCV/CuNPs. When specified in the text, oxygen was removed from the electrolyte by bubbling with purified nitrogen for 30 min. A blanket of nitrogen was subsequently kept over the solution during measurements.

3. 3 Results and discussion

3.1. Copper coordination on the chelating electrode based on PCV

Initially, the chelated electrode in this work was constructed by electrodeposition of PCV at SWCNTs modified GCE by potential cycling between −0.2 and 0.5 V vs. SCE at 20 mV s^{-1} and the electrolytic solution consisting of 1 mM PCV in 0.1 M PBS (pH 7). The cyclic voltammograms (CVs) obtained during electrodeposition of PCV are shown in inset of Fig. 1. Highly reversible redox peaks of PCV monomer can be observed at 0.05 V. An anodic peak appears at 0.20 V due to oxidation of catechol to *o*-benzoquinone which upon subsequent cathodic scan gets reduced to catechol at 0.147 V following a quasi-reversible two-electron process ($E^{0'}$ = 0.174 V) with a peak to peak separation of 53 mV. The second and subsequent potential sweeps show a decrease in current of redox couple at 0.174 V due to the adsorption of oxidation products. Further oxidation of PCV becomes more and more difficult because the diffusion of PCV molecules from the bulk solution towards the electrode surface has to take place through the layer of adsorbed catechols [20,21]. These adsorbed catechols can provide accessible site for the preconcentration of copper ions.

The coordination of copper ions with SWCNTs and SWCNTs/PCV modified electrodes were carried out by immersing the modified electrodes for 15 min in sodium acetate/acetic acid buffer solution (pH 4.5) containing 0.01 M copper nitrate or lead nitrate under stirring conditions. After accumulation of the metal ions, the