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Non-enzymatic detection of hydrogen peroxide based on Fenton-type reaction on poly(azure A)-chitosan/Cu modified electrode

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ABSTRACT

In this work, a sensitive electrochemical method for the detection of H_2O_2 was proposed based on Fenton-type reaction on the electrode surface. A glassy carbon electrode modified with poly(azure A) (PAA), chitosan (CS) and copper ions, displaying a good electrochemical activity, was fabricated by cyclic voltammetry and the adsorption of Cu^{2+}. Scanning electron microscopy-Energy dispersive spectroscopy analysis, infrared and Raman spectral characterization and XPS measurement showed the stable complexation of Cu^{2+} with the PAA-CS film. Hydroxyl radicals derived from the Fenton-type reaction between Cu^{2+} and H_2O_2 could effectively oxidize poly(azure A), leading to the great reduction-current change of the dye polymer in the electrode process. Under the optimized conditions, the fabricated electrode displayed a linear response in the H_2O_2 concentration range from 0.002 to 0.5 mM and that from 2.56 to 25.0 mM with a detection limit of 0.7 μM estimated at a signal-to-noise ratio of 3. The good analytical performance including low detection limit, fast response time, low cost, good anti-interference performance, satisfying stability, acceptable repeatability and reliable reproducibility were found from the proposed amperometric sensor, suggesting that the current work could provide a feasible approach for the non-enzymatic H_2O_2 detection.

1. Introduction

The history of Fenton chemistry is able to date back to 1876 when H. J. H. Fenton described a colored product obtained by mixing tartaric acid with hydrogen peroxide and a low concentration of ferrous salt [1]. The occurrence of hydroxyl radical (•OH) in Fenton reaction between H_2O_2 and Fe^{2+} has been suggested [2]. As a strong oxidizer with a high oxidation potential of 2.8 V, which is only inferior to fluorine in oxidation nature [3],•OH is able to react with practically all classes of organic compounds, leading to either degradation of these compounds or their conversion into less aggressive products [4,5]. Fenton chemistry has found its actual applications in some fields. For example, Fenton's reagent can be used to degrade toxic organic compounds presented in a medium including wastewater and soil [6,7].

The spectrophotometric determination of some trace metal ions, such as copper(II) [8], aluminum(III) [9], manganese(II) [10], chromium(VI) [11], titanium(IV) [12], cobalt(II) [13], ruthenium (III) [14], palladium [15], vanadium(V) [16], molybdenum(VI) [17], and etc., based on their catalytic activity on the oxidation of organic dyes by hydrogen peroxide has been reported. One can find that the oxidation ability of H_2O_2 in the presence of metal ions is far superior to that in the absence of these catalyzers. In addition, high sensitivity is usually accompanied by poor selectivity due to the similar catalytic effects of several transition metal ions. Up to now there is still no consensus on the specific reaction mechanism. A reasonable interpretation focuses on the Fenton-type reaction of H_2O_2 with metal ions and the function of •OH as a strong oxidizer [18].

Hydrogen peroxide is an important material in many fields including industry, environment, food and medicine. Biologists reveal that hydrogen peroxide plays an important role as a signaling molecule in the regulation of a wide variety of biological processes [19]. The compound can decompose into hydroxyl radicals that readily react with and damage vital cellular components [20]. It is found that cell injury through base modifications and strand breakage in genomic DNA [21] as well as apoptosis induction [22] are closely related to accumulation of H_2O_2. Free hydrogen peroxide may damage any tissue it encounters via oxidative stress, which has been proposed as a cause of cancer

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[23]. Not a few researchers devote themselves to develop some H_2O_2 sensors with low cost, high sensitivity and good biocompatibility. The amperometric H_2O_2 sensors, which exhibit the current-signal change after introduction of H_2O_2, usually comprise two types. One is prepared based on the direct electrochemistry of H_2O_2 on electrode surfaces modified with noble metal nanomaterials [24,25], metal alloys [26], metal oxides [27], carbon nanotubes [28], graphene [29], and etc. The other employs immobilized catalyzers, which are subdivided into two classes, biomacromolecules (horse radish peroxidase [30], haemoglobin [31] and myosin [32], and etc.) and electroactive materials (Mn [33], Cu [34], organic dye [35], dye polymer [36], and etc.) acting as mimic enzymes.

It is mentioned that many organic compounds can be oxidized effectively by H_2O_2 in the presence of some metal ions. So we surmise that a valid electrochemical H_2O_2 sensor can be fabricated by employing organic dye polymer with electroactivity and transition metal ions. In this paper, a glassy carbon electrode modified by poly(azure A)-chitosan/copper ion composite film was prepared and the electrode surface was characterized by scanning electron microscopy-Energy dispersive spectroscopy (SEM-EDS) analysis, infrared spectral characterization and Raman spectral measurement. The catalytic ability of several modified electrodes for the reduction of H_2O_2 was compared and some factors including the different metal ions immobilized on the electrode surface, the concentration of Cu^{2+} solution, the adsorption time of Cu^{2+} and pH, which could affect Fenton-type reaction and detection sensitivity, were all investigated. The linear range, detection limit, anti-interference performance, stability and reproducibility of the developed non-enzymatic H_2O_2 sensor were evaluated, respectively.

2. Experimental

2.1. Materials and apparatus

Azure A (B.S., dye content >99%) was purchased from Xiya Chemical Industry Co., Ltd. (Linshu, China). Chitosan (CS, from crab shells, >90% deacetylation) was obtained from Shanghai Biochemical Reagents Co., Ltd. (Shanghai, China). The 5 mM azure A solution was obtained by dissolving the dye with 0.1% CS. Copper sulphate (A. R.) and hydrogen peroxide (30%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The hydrogen peroxide stock solution was prepared daily to avoid its excessive decomposition to water and oxygen, which is accelerated when the solution is diluted. Ascorbic acid (AA, Z99.0%, Fluka), dopamine (DA, Aldrich) and uric acid (UA, Aldrich) were used as received. The buffer for the assay was 0.1 M pH 7.0 phosphate buffered saline (PBS), prepared by mixing stock standard solutions of Na_2HPO_4 and KH_2PO_4. Other chemicals were of analytical reagent grade and all aqueous solutions were prepared in Milli-Q ultrapure water.

Electrochemical measurement experiments were performed with a CHI660C electrochemical workstation (CH Instruments, China) by using a three-electrode electrolytic cell. Glassy carbon electrode (GCE, 3 mm in diameter) acted as the working electrode. A KCl saturated calomel electrode (SCE) served as the reference electrode (RE). A platinum plate served as the counter electrode (CE). Scanning electron microscopy-Energy dispersive spectroscopy (SEM-EDS) analysis of the modified electrode surfaces were performed on a Nova NanoSEM 230 field-emission scan electron microscope (FEI, USA). A Nicolet Nexus 670 FTIR spectrometer (Nicolet, USA) was employed for the infrared spectral analysis. A DXR Raman Microscope (Thermo Scientific, USA) was used for the Raman spectral measurement. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi X-ray Photoelectron Spectrometer (Thermo Fisher, UK).

2.2. Preparation of the chemically modified electrode and measurement procedure

Prior to modification, GCE was polished with 0.05 μm α-Al_2O_3 power slurries until a mirror shiny surface appeared, and it was sonicated sequentially in acetone, HNO_3 (1:1, v/v), NaOH (1 M) and ultrapure water for 3 min. The treated electrode was scanned between −1.0 and 1.0 V versus SCE in 0.5 M H_2SO_4 aqueous solution for sufficient cycles to obtain reproducible cyclic voltammograms. After the electrode was thoroughly rinsed with ultrapure water and dried with a stream of nitrogen gas, 5 μL of azure A-CS mixture solution was dropped on the GCE surface and allowed to dry at room temperature (25 °C). The electropolymerization of azure A was initiated in a N_2-saturated 0.1 M pH 6.5 PBS by cyclic voltammetry from −1.0 to 1.8 V for 3 cycles with a scan rate of 100 mV s^{-1}. The poly(azure A)-chitosan (PAA-CS) film was then grown in the same solution by potential cycling between −0.6 and 0.5 V at 100 mV s^{-1} for 30 cycles. Next, the prepared electrode, which was marked as GCE/PAA-CS, was immersed in 1 mM $CuSO_4$ solution for 60 minutes. Finally, the obtained electrode was thoroughly rinsed with ultrapure water and dried with a stream of nitrogen gas. The prepared electrode was defined as GCE/PAA-CS/Cu. All electrochemical detections were carried out at room temperature in 0.1 M PBS as the supporting electrolyte. Cyclic voltammetry (CV) measurements were carried out from −0.6 to 0.8 V at a scan rate of 100 mV s^{-1}. Amperometric measurements were performed under a stirring condition with increasing of H_2O_2 concentration. All solutions tested were thoroughly deoxygenated by bubbling pure nitrogen gas, and a continuous flow of nitrogen gas was maintained over the solution during experiments.

3. Results and Discussion

3.1. Preparation of GCE/PAA-CS and its electrochemical response to H_2O_2

In this work, the PAA-CS modified GCE was obtained by a two-step electropolymerization after the AA-CS film was cast on the bare GCE surface. The initial cyclic voltammetric scan in a N_2-saturated 0.1 M pH 6.5 PBS from −1.0 to 1.8 V could result in the oxidation of NH_2 groups of the azure A molecule, producing the cation radicals [37], which was necessary to the formation of the dye polymer. Fig. 1A displays the respective growth process of the PAA-CS film on GCE surface via consecutive potential cycling between -0.6 and 0.5 V in a N_2-saturated 0.1 M pH 6.5 PBS. Two pairs of redox peaks on the CV curves, in which the peak currents at lower (more negative) potential (I-I′) were relatively higher, were observed and the peak currents were increased with the successive cycles, suggesting that azure A suffered electropolymerization and the dye polymer was successfully generated on the electrode surface in the presence of chitosan. The cyclic voltammetric scan of the PAA-CS film modified GCE in pH 7.0 PBS at various scan rates was performed and the results are shown in Fig. 1B. With the rise of the scan rate, the anodic peaks shifted positively but the cathodic peaks moved negatively. Both the anodic and cathodic peak currents were directly proportional to the scan rate, demonstrating a surface controlled electrode process. Similar results have been determined in previous studies on the PAA modified electrode in the absence of chitosan [38,39].

Fig. 2 shows that the cyclic voltammograms of GCE/PAA, GCE/CS and GCE/PAA-CS in 0.1 M pH 7.0 PBS in the absence and presence of H_2O_2. As shown in the panel A, a pair of redox peaks (I-I′) at about −0.21 V and −0.33 V as well as two shoulder peaks (II-II′) at about