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Nanomolar detection of hydrogen peroxide at a new polynuclear cluster of tin pentacyanonitrosylferrate nanoparticle-modified carbon ceramic electrode

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ABSTRACT

This work describes a new electrochemical sensor for hydrogen peroxide based on tin pentacyanonitrosylferrate (SnPCNF)-modified carbon ceramic electrode (CCE). The modified electrode was constructed by using a sol–gel technique involving two steps: construction of CCE containing metallic tin (Sn) powder and then electrochemical creation of SnPCNF film on the surface of CCE. The modified electrode was characterized by energy-dispersive X-ray, Fourier transform infrared, scanning electron microscopy, and cyclic voltammetry (CV) techniques. The charge transfer coefficient (α) and charge transfer rate constant (k_s) for the modifying film were calculated. The electrocatalytic activity of the modified electrode toward the reduction of hydrogen peroxide was studied by CV and chronoamperometry. A linear calibration curve was obtained over the hydrogen peroxide concentration range of 0.5 to 69.4 μM using a hydrodynamic amperometric technique. The limit of detection (for a signal-to-noise ratio of 3) and sensitivity were found to be 92 nM and 0.89 μA/μM, respectively. Furthermore, the diffusion coefficient of hydrogen peroxide (D) and catalytic rate constant (k_{cat}) were calculated.

Because of wide industrial applications of hydrogen peroxide as a general oxidant and its important role in many different fields, such as clinical, food, pharmaceutical, and environmental analysis [1], its detection with a reliable, rapid, and economic method is a necessity. Moreover, hydrogen peroxide is a very important intermediate in biological reactions, and by means of the quantitation of its production in enzymatic reactions as one of the reaction products [2], other compounds such as cholesterol, glucose, and triglyceride can be determined [3,4].

Among different techniques, the electrochemical methods have been found to be suitable for rapid, accurate, and economical monitoring of hydrogen peroxide [5]. The use of bare electrodes for this purpose is not appropriate because direct oxidation or reduction of hydrogen peroxide at common electrodes has slow kinetics and requires high overpotentials. Modification of electrode surface with chemical modifiers is one of the possible approaches to overcome the problems mentioned above. Various modified electrodes have been established as electrochemical sensors for hydrogen peroxide sensing.

Recently, much attention has been paid to constructing third-generation biosensors for hydrogen peroxide based on enzymes such as myoglobin, horseradish peroxidase [6], and hemoglobin [7]. However, difficult immobilization and biological instability of enzymes are the major drawbacks related to the use of enzymes in electrochemical biosensors. To eliminate these drawbacks, non-enzymatic modifiers have been widely used.

The most common kinds of these modifiers used for constructing hydrogen peroxide biosensors are based on organic mediators such as Nile Blue, quinines [8,9], numerous metal complexes [10], and transition metal phthalocyanines [6].

In addition, metal hexacyanoferrates (MHCFs)[1] have been considered as another class of interesting materials for the electrocatalysis of H_2O_2. Metal cyanoferrates are one of the most important groups of inorganic compounds used for electrode modification. Due to their interesting properties, such as chemical stability, highly reversible nature of electrode reactions, easy preparation, and low cost, they have been widely used for different practical applications, including electrochromic devices [11], sensors [12], and electrocatalysis [13]. Iron(III) hexacyanoferrate(II) is the first model of transition metal cyanoferrate (commonly known as Prussian Blue [PB]) that was reported by Neff in 1978 [14]. A lot of H_2O_2 sensors based on PB-modified electrodes [15–17] have been reported. Also, cobalt(II) hexacyanoferrate- and chromium(III) hexacyanoferrate-modified glassy carbon (GC) electrodes have been used as amperometric H_2O_2 sensors [18].

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[1] *Abbreviations used:* MHCF, metal hexacyanoferrate; PB, Prussian Blue; GC, glassy carbon; PCNF, pentacyanonitrosylferrate; NP, nitroprusside; Pt, platinum; SnPCNF, tin pentacyanonitrosylferrate; CCE, carbon ceramic electrode; MTMOS, methyltrimethoxysilane; Sn, tin; SCE, saturated calomel electrode; FTIR, Fourier transform infrared; SEM, scanning electron microscopy; EDX, energy dispersive X-ray; IR, infrared; CV, cyclic voltammetry.

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The preparation and electrochemical behavior of some PB analogue-modified electrodes have been reported based on different transition MHCFs [19–21]. Pentacyanonitrosylferrate (PCNF) is a member of the polycyanide metal complexing reagents that is referred to as nitroprusside (NP). Based on the results reported by Gao and coworkers [22], NP was successfully used for the preparation of copper PCNF on the platinum (Pt) and GC electrodes and cobalt PCNF on a GC electrode [23]. To extend the electroanalytical methods based on the modified electrode, some research activities have been oriented on the electrochemical synthesis of mixed transition MHCFs [24,25] and rare earth hexacyanoferrates [26]. In this field, to the best our knowledge, there has been no report about the preparation or application of tin pentacyanonitrosylferrate (SnPCNF)-modified electrode. A part of the current work describes a simple method to create SnPCNF film on the carbon ceramic electrode (CCE).

Besides the kind of modifying film, the nature of electrode substrate is also an effective factor on electrocatalytic properties of modified electrodes because it affects the morphologies of modifying film as well as its electrocatalytic properties. Here, considering the interesting features of CCE, such as renewable surface, high conductivity, stability, porosity, wide operational potential window, and good mechanical properties [27,28], we used it as a substrate for electrochemical deposition of SnPCNF film. The CCE was prepared by the sol–gel technique. Sol–gel technology has aroused great interest in designing and applying electrochemical sensors and electroanalysis due to its simplicity, stability, physical rigidity, transparency, permeability, versatility, flexibility, and low cost in the preparation procedure [29]. Lev and coworkers [30] proposed the sol–gel process conducted in the presence of graphite powder for fabricating CCEs as a new kind of chemically modified electrodes.

The second part of the current work was aimed at surveying the electrochemical properties and electrocatalytic activity of SnPCNF film toward the reduction of hydrogen peroxide in weak acidic solutions. Considering the weak acidic nature of H_2O_2 samples in food industry and environmental analysis, direct determination of it in acidic solutions is very worthwhile [31,32] and attempts to find suitable electrocatalysts for low-potential determination of hydrogen peroxide with high sensitivity are of major importance in biological and chemical samples.

Materials and methods

Reagents

Methyltrimethoxysilane (MTMOS) was obtained from Fluka. Potassium nitrate, methanol, acetic acid, HCl, KOH, H_2SO_4, H_2O_2, Tin (Sn) powder, fine powdered graphite, and sodium pentacyanonitrosylferrate were obtained from Merck. A developer cream containing hydrogen peroxide (Collection, Sharmel, France), which is used for hair coloring, was obtained from a local pharmacy. All solutions were prepared with distilled water.

Apparatus

An Autolab PGSTAT-100 potentiostat/galvanostat equipped with a USB electrochemical interface and driven by GPES software was used for electrochemical experiments. A conventional three-electrode cell was used at room temperature. The modified CCE (3.9 mm diameter) was used as the working electrode. A saturated calomel electrode (SCE: $Hg|Hg_2Cl_2$, KCl 3 M) and a Pt wire were used as the reference and auxiliary electrodes, respectively. The Fourier transform infrared (FTIR) spectra were recorded using a Bruker model Vector 22 FTIR spectrometer. The scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analyses were also carried out using a scanning electron microscope (LEO 440i, Oxford) equipped with an EDX microanalyzer.

Electrode preparation

The two-step sol–gel processing method was used for fabricating SnPCNF-modified CCE according to the following procedure. At the first step, a portion of 0.3 ml of MTMOS was mixed with 0.45 ml of methanol and 10 μl of 11 M HCl as catalyst. The mixture was magnetically stirred for approximately 3 min until a clear and homogeneous solution resulted. Then 0.3 g of graphite powder and 0.03 g of metallic Sn powder were added, and the mixture was shaken for an additional 1 min. Subsequently, the homogenized mixture was firmly packed into a Teflon tube (with 3.9 mm i.d. and 10 mm length) and dried for at least 24 h at room temperature. A copper wire was inserted through the other end to set up electric contact. The electrode surface was polished with emery paper (grade 1500) and rinsed with distilled water. At the second step, the CCE containing metallic Sn was immersed in a 0.02-M PCNF solution and derivatized by cycling the electrode potential between −0.3 and 1.3 V with a scan rate of 50 mV s^{-1} for 1 h. To reach a morphological stabilization of the crystal lattice of the film, the modified electrode was stored in air for at least 1 day. The SnPCNF film formation can be shown as follows:

$$\text{During anodic scan: } (1/2)\ \mathrm{Sn} + [\mathrm{Fe(CN)_5NO}]^{2-} + \mathrm{K^+} \rightarrow \mathrm{KSn^{II}_{0.5}[Fe(CN)_5NO]} + e^- \quad (1)$$

$$\text{During cathodic scan: } \mathrm{KSn^{II}_{0.5}[Fe(CN)_5NO]} + e^- + \mathrm{K^+} \rightarrow \mathrm{K_2Sn^{II}_{0.5}[Fe(CN)_5NO]} \quad (2)$$

When the electrode potential is anodically swept in the presence of solution species of $[Fe(CN)_5NO]^{2-}$, NP(II), the metallic Sn doped in CCE is oxidized to Sn (II) and forms insoluble compound $KSn^{II}_{0.5}[Fe(CN)_5NO]$ at the electrode surface. It is considerable that the initial $[Fe(CN)_5NO]^{2-}$ in reaction layer may be partially reduced to $[Fe(CN)_5NO]^{3-}$, NP(III) by applying a negative potential of −0.3 V, but its main form, NP(II), is regenerated during the positive scan.

Results and discussion

Physicochemical characterizations of the modified electrode

Fig. 1A shows the SEM image of a bare carbon ceramic surface immediately after polishing with emery paper (grade 1500). As seen in this image, the surface is dense and scaly and has a high porosity. During the modification of CCE, the SnPCNF particles are being formed with an average size of approximately 100 nm (Fig. 1B). To verify the composition of the synthesized SnPCNF samples, the FTIR spectrum is recorded. Fig. 2A shows a typical FTIR spectrum of SnPCNF samples. The sharp peak at 2079 cm^{-1} is related to stretching frequency of —C≡N ligand existing in the solid structure of SnPCNF. Focusing on the FTIR spectra shows that the stretching vibration of the C≡N group in SnPCNF film is singlet. This indicates that there is one stoichiometric compound in the SnPCNF system [33,34]. The absorption bands at 3422 and 1636 cm^{-1} are assigned to the O—H stretching and bending vibration, respectively, of crystal water present in the structure of the SnPCNF samples. So, it can be said that SnPCNF is a hydrous film. All results of the infrared (IR) spectrum confirm the existence of SnPCNF thin film on the surface of CCE. Also, the observed frequency at 2854 and 2925 cm^{-1} can be attributed to the stretching vibrations of sp^3 C—H related to —CH_3 groups at the surface of CCE