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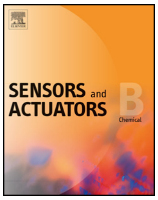

Iron oxide nanorods array in electrochemical detection of H_2O_2

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ABSTRACT

Nanorod arrays (NRs) of β-FeOOH, γ-Fe_2O_3, and α-Fe_2O_3 were synthesized, and their electrocatalytic properties toward the reduction of H_2O_2 were investigated. In phosphate electrolyte, iron phosphate ($FePO_4$) was *in situ* deposited onto these iron oxides during pretreatment, and the interaction between iron oxides and the deposited $FePO_4$ played an important role in determining the electrocatalytic activity of the resultant electrodes. It was found that the redox reaction of $FePO_4$ is more facile on α-Fe_2O_{3NR}, and the resultant $FePO_4$ modified α-Fe_2O_{3NR} showed best electrocatalytic activity toward the reduction of H_2O_2. In addition, α-Fe_2O_{3NR} showed two reduction peaks in phosphate electrolyte containing 1.66 mM H_2O_2, one being pH-dependent and related to the electrocatalytic properties of $FePO_4$, and the other one being pH-independent and only related to the intrinsic electrocatalytic properties of α-Fe_2O_{3NR}. However, all iron oxides showed only one pH-independent reductive peak in non-phosphate electrolyte containing H_2O_2. The sensing mechanisms in both conditions are proposed. Under optimized condition, α-Fe_2O_{3NR} exhibited excellent sensing characteristics, including a high sensitivity of 181 $\mu A\,mM^{-1}\,cm^{-2}$, a wide linear range up to 2.5 mM, a low detection limit of 1.3 μM, and high selectivity against some common biomolecules, which indicates its applicability as a reliable electrochemical H_2O_2 sensor.

1. Introduction

Hydrogen peroxide (H_2O_2) is a chemical widely used in food and chemical industries [1]. In addition, it is a frequent intermediate involved in many enzymatic processes. Therefore, the quantitative detection of H_2O_2 is of great importance in these fields. Several methodologies, including chemiluminescence [2], spectrophotometry [3], fluorometry [4], and electroanalytical techniques [5–16], have been developed for the detection of H_2O_2. Among them, the amperometry offers advantages, including simplicity, low cost, rapidness, and real-time monitoring, and has been considered as the most promising approach for H_2O_2 detection.

H_2O_2 can be electrochemically oxidized or reduced. Nevertheless, the detection of H_2O_2 by measuring the current from the reduction of H_2O_2 is preferential for biological samples as the detection is free from interferences caused by bio-molecules, such as ascorbic acid and uric acid, which are present in large quantity in biological samples [17,18]. On the other hand, to develop the electrochemical H_2O_2 sensor with high sensitivity, a suitable electrocatalyst, which can effectively catalyze the reduction of H_2O_2, is required.

Since the discovery of the size-dependent peroxidase-like activity of magnetite (Fe_3O_4) nanoparticles [19], iron oxide based materials for the electrochemical detection of H_2O_2 have been intensively studied. So far, magnetite [9,16], various structural forms of ferric oxides (*e.g.*, α-Fe_2O_3 [5,6,10,15], and γ-Fe_2O_3 [11,12,14]), and ferric oxyhydroxides [15] have been explored as active and stable material catalyzing H_2O_2 reduction electrochemically. However, the active species and key factors (*e.g.*, particle size, shape, *etc.*) responsible for the catalysis of H_2O_2 reduction are still not well-understood. For example, the electrocatalytic activity of iron oxides nanoparticles, including ferrihydrite, γ-Fe_2O_3, β-Fe_2O_3, α-Fe_2O_3, and amorphous Fe_2O_3, have been investigated and compared previously [5], and the authors found that the amorphous Fe_2O_3 showed best electrocatalytic activity. Nevertheless, the electrocatalytic activity of these iron oxide nanoparticles were not compared at the same size, and the mechanism for enhanced electrocatalytic activity of amorphous Fe_2O_3 was not elucidated. On the other hand, various nanostructures of iron oxides have also been synthesized, such as nanorods [15] nanoparticles [5,10–16], and nanotubes [6], and these nanostrucutres have been shown to enhance the electrocatalytic activity of iron oxides. Nevertheless, these nanostructured iron oxides were rarely directly deposited onto the electrode surface. Instead, they were synthesized in powder form [5,6,10–16] and required additional coating procedure and

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optimization procedure (*e.g.*, carbon paste content [5,12]) for electrode preparation, which complicates the electrode preparation procedure.

In this report, we report the directly growth of iron oxides onto Fluorine-doped tin oxide coated glass substrate (FTO) using a simple and scalable chemical bath deposition (CBD) at mild conditions. β-FeOOH nanorod array (β-FeOOH$_{NR}$) was first directly grown onto the FTO substrate, and its conversion into nanorod arrays of maghemite (γ-Fe$_2$O$_{3NR}$) and hematite (α-Fe$_2$O$_{3NR}$) was achieved by annealing at 300 °C and 500 °C for 30 min, respectively. The electrocatalytic properties of these nanostructured iron oxides toward the reduction of H_2O_2 were investigated and compared in different electrolytes. With the same nanostructure and similar size, the difference in electrocatalytic activity can truly reflect the intrinsic properties of these iron oxides, allowing us to directly investigate the role of the crystal phase/chemical composition of these iron oxides played in their electrocatalytic activity. It was found that hematite nanorods array exhibited highest activity toward electrochemical reduction of H_2O_2. Finally, the excellent performances obtained from sensitivity test, the interference test, and the long-term stability test, indicate the applicability of α-Fe$_2$O$_{3NR}$ for amperometric detection of H_2O_2.

2. Experimental

2.1. General consideration

Starting materials for the synthetic part of the work were purchased from commercial suppliers and of the highest available purity for the analytical work. Flourine-doped tin oxide (FTO) coated glass (sheet resistance 7 Ω sq^{-1}, TEC GlassTM 7) substrates (1.0 cm × 3.0 cm) were cleaned with an ammonia-hydrogen peroxide-deionized water mixture (volume ratio: 1:1:5) at 70 °C for 30 min, after which the FTO substrates were dried at room temperature under nitrogen purge. Hydrogen peroxide stock solution (0.5 M) was prepared before each experiment by direct dilution of hydrogen peroxide (H_2O_2, 30 wt%) with electrolyte solutions, of different pHs, containing (i) sodium phosphate (0.1 M) and sodium sulfate (0.1 M) or (ii) sodium sulfate (0.1 M). Uric acid (>99%, Sigma), Dopamine hydrochloride (Sigma), and ascorbic acid (>99%, Sigma) were used for the interference test. Deionized water (DIW) was used throughout the work.

2.2. Preparation of the nanostructured iron oxides based modified electrodes

The maghemite (γ-Fe$_2$O$_3$) and hematite (α-Fe$_2$O$_3$) nanorods (NRs) modified electrodes were prepared by first growing akagenite (β-FeOOH) NRs onto the FTO substrate (exposed area of 2.0 cm^2) using chemical bath deposition (CBD) in an aqueous solution containing urea (6.25 wt%) and iron chloride (0.15 M), followed by annealing at 300 °C and 500 °C, respectively, for 1 h. The akagenite, maghemite, hematite NRs modified electrodes were designated as FTO|β-FeOOH$_{NR}$, FTO|γ-Fe$_2$O$_{3NR}$, and FTO|α-Fe$_2$O$_{3NR}$, respectively.

2.3. Physical characterization

The surface morphology of the electrodes was characterized using a Hitachi SU-8010 scanning electron microscope (SEM). X-ray diffraction (XRD) analyses were carried out using an Ultima IV (Rigaku Co., Japan) X-ray diffractometer. The surface composition of the films was verified by X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe system, ULVAC-PHI, Chigasaki, Japan), using a microfocused (100 μm, 25 W) Al X-ray beam, with a photoelectron take off angle of 45°. The Ar$^+$ ion source for XPS (FIG-5CE) was controlled by using a floating voltage of 0.2 kV. The binding energies obtained in the XPS analyses were corrected for specimen charging, by referencing the C 1s peak to 285.0 eV.

2.4. Electrochemical measurement

Electrochemical characterizations on the electrocatalytic properties of the modified electrodes were performed with an Autolab PGSTAT 204 (Eco Chemie B.V.) at room temperature and all potentials are reported against Ag/AgCl (saturated KCl). A conventional three-electrode electrochemical cell was employed with FTO|β-FeOOH$_{NR}$, FTO|γ-Fe$_2$O$_{3NR}$, or FTO|α-Fe$_2$O$_{3NR}$ (exposed area of 1.0 cm^2) as the working electrode, Pt foil (exposed area 4.0 cm^2) as counter electrode, and Ag/AgCl as reference electrode.

Prior to experiments, all modified electrodes were pretreated either in (i) phosphate buffer solution (PBS) containing sodium phosphate (0.1 M) and sodium sulfate (0.1 M), or in (ii) sodium sulfate (0.1 M), using cyclic voltammetry (CV) at a scan rate of 50 mV s^{-1} in the potential window between −0.7 V and +0.4 V (*vs.* Ag/AgCl) for 20 cycles. The pH of both solutions was kept 7. A suitable operating potential in the limiting current plateau region for the amperometric detection of H_2O_2 was determined using linear sweep voltammetry (LSV) at a scan rate of 0.1 mV s^{-1} in PBS (pH 6) containing 0 mM and 4.95 mM H_2O_2. After obtaining the operating potential, which is −0.3 V *vs.* Ag/AgCl, the amperometric detection of H_2O_2 was carried out in PBS (pH 6) under constant magnetic stirring. The current density responses to the changes H_2O_2 concentration were collected, and the calibration curve for detection of H_2O_2 was then constructed.

3. Results and discussion

3.1. Physical characterization

Fig. 1a shows the X-ray diffraction patterns of akagenite annealed at different temperatures. It can be found that the akagenite (JCPDS No. 34-1266) converted into maghemite (JCPDS No. 39-1346) and hematite (JCPDS No. 89-0599) after being annealed at 300 °C and 500 °C, respectively. In addition, as revealed in Fig. 1b–d, the synthesized akagenite consists of uniform nanorods with length of ~600 nm and diameter of about 40 nm, and the annealing procedure did not cause any obvious change in surface morphology, which allows us to directly investigate the effects of chemical composition/phases of iron oxides on their electrocatalytic properties toward the reduction of H_2O_2 without considering the morphology effect.

3.2. Effects of phosphate ions on electrochemical behaviors during pretreatment

The 20-cycle CV curves of the FTO|α-Fe$_2$O$_{3NR}$ electrode recorded at 50 mV s^{-1} during the CV treatment in PBS (pH 7) are shown in Fig. 2. An irreversible cathodic wave with onset potential of −0.15 V *vs.* Ag/AgCl in the first forward scan, which can be attributed to the reductive dissolution process of hematite (Eq. (1)): [20]

$$Fe_2O_{3(s)} + 6H^+_{(aq)} + 2e^- \rightleftarrows 2Fe^{2+}_{(aq)} + 3H_2O_{(l)} \quad (1)$$

In the following cycles, reversible redox peaks, with midpoint potential (E_{mid}) of ~−0.27 V *vs.* Ag/AgCl, appeared, grew, and became saturated after 20-cycle scans. After pretreatment, the pretreated FTO|α-Fe$_2$O$_{3NR}$ electrode was rinsed with DIW and subjected to further electrochemical studies. Fig. 3 shows the CVs of the pretreated FTO|α-Fe$_2$O$_{3NR}$ electrode in the PBS (pH 7) at different scan rates. It was found that the CV responses are retained and the relationship between the peak cathodic current density (I_{pc}) with scan rate (ν) is linear, suggesting an electroactive species