Efficient electrocatalytic reduction and detection of hydrogen peroxide at an Ir^{IV}Ox·H$_2$O nanostructured electrode prepared by electroflocculation

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ABSTRACT

An Ir^{IV}Ox·nH$_2$O nanostructured electrode prepared by electroflocculation is reported; the electrode efficiently catalyzes the electrochemical reduction of hydrogen peroxide (H$_2$O$_2$). Linear sweep voltammograms reveal that the potential onset arising due to the reduction of H$_2$O$_2$ (1 mM) occurs at -0.1 V (vs. Ag/AgCl), which is more anodic than the onset potential occurring on the glassy carbon electrode by 400 mV, thereby substantiating the catalytic utility of Ir^{IV}Ox·nH$_2$O. The number of electrons transferred in the process, estimated via the Koutecky-Levich equation, is 1.89 ± 0.30. The Tafel slope obtained from polarization measurements is ca. 240.9 mV/dec. Furthermore, the Ir^{IV}Ox·nH$_2$O nanostructured electrode exhibits response with linear relationship against H$_2$O$_2$ concentrations ranging over 0-1 mM (when agitated) and 0-150 μM (in flow injection analysis); the limit of detection (3σ), as determined under flow injection analysis, is 5 μM. The as-fabricated electrode is insensitive to the oxidation of ascorbic acid (0.1 mM) and acetaminophen (0.1 mM) and exhibits stable amperometric response (over twenty successive trials), albeit a slight drift in the sensor response is observed during the initial six evaluations. Based on the results, the electrocatalytic mechanism involving the following steps is proposed: (1) the reduction of Ir from Ir^{IV} to Ir^{III}, (2) catalytic cleavage of the O-O bond to generate OH$^{\bullet}$ radicals, and (3) the reduction of the OH$^{\bullet}$ radicals to OH^{-} via the reoxidation of Ir^{III} to Ir^{IV}.

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1. Introduction

Hydrogen peroxide (H$_2$O$_2$) is one of the most widely-utilized basic chemicals in a broad variety of industrial applications such as chemical synthesis, food processing and packing, cosmetic and pharmaceutical manufacture, paper and textile bleaching, among others [1]. In biological aerobic organisms, reactive oxygen species (OH$^{\bullet}$, O$_2^{\bullet}$, and H$_2$O$_2$) are generated via the energy metabolism in the cellular mitochondria [2,3]. High levels of reactive oxygen species has been shown to cause illness such as atherosclerosis, myocardial infarction, Parkinson disease, and Alzheimer disease [4–7]. In the field of biosensors, determination of H$_2$O$_2$ has attracted considerable research interest by virtue of its presence as either an intermediate or product of enzymatic reactions [8–11]. Thus exploiting efficient method to analyze concentration of H$_2$O$_2$ is being continuously proceeded.

Despite significant progress that has been made towards the realization of high-fidelity H$_2$O$_2$ analysis using various methods

[12–17], the electrochemical redox detection technique remains one of the most popular mechanisms owing to its high sensitivity and efficiency. The electrochemical method is also considered comparatively inexpensive and straightforward to implement and operate. Numerous single- and multi-component metallic catalysts have been investigated to catalyze the electrochemical oxidation of H$_2$O$_2$, including Cu [18], Fe [19], and Ir [20–22]. However, a key challenge arises using such metallic species – the concurrent oxidation of interfering substances, thereby serving to deteriorate accurate determination of levels of H$_2$O$_2$. Metals or alloys containing Cu [23,24], Ag [25], Pt [26], Pd [27], and Ir [20,28,29] have thus been used as the electrode material of choice to catalyze the reduction of H$_2$O$_2$.

Of these catalysts, iridium (Ir) and iridium oxide (IrOx) have been investigated as promising electrode materials, both of which offer several advantageous features including high stability [30,31] with exceptional resistance against dissolution and corrosion, reversible redox properties [32,33] owing to multiple redox states (III/IV/V/VI), good biocompatibility [34–36] for use in implantable devices, and exceptional matrix properties for the immobilization of enzymes [22,37–40]. To facilitate the detection of H$_2$O$_2$ using IrOx, electrodes were prepared by the electrochemical oxidation of

Ir [20,37], thermal decomposition of a precursor solution containing Ir^{IV} [29], and electrodeposition on a glassy carbon electrode (GCE) in a solution containing PdCl$_2$ and NaIrCl$_6$ [41–43]. While Cox et al. has proposed that IrOx serves as a superior catalytic species towards H$_2$O$_2$ reduction based on a mediation mechanism [41], the efficiency of electrocatalytic H$_2$O$_2$ reduction was still highly dependent on the underlying electrode substrate [20], hence inferring that the underlying Ir played a dominant role in the electrode's catalytic ability.

Recently we reported a method using electro-flocculation [44], which harnesses a dual-potential pulsed amperometric (DPPA) technique to expedite water oxidation (1.3 V) and oxygen reduction (-0.7 V) reactions intermittently, depositing Ir^{IV}Ox·nH$_2$O onto a GCE in well-dispersed nanostructures (Fig. S1). The resulting Ir^{IV}Ox·nH$_2$O nanostructured electrode exhibits high resistance to acidic and alkaline solutions over a wide potential window. Analysis of the resulting Ir^{IV}Ox·nH$_2$O film using X-ray photospectrometry indicates that the constitution of the film is mainly Ir^{IV} oxide; metallic Ir was mostly absent (Fig. S2). This enables us to investigate the electrocatalytic reduction of H$_2$O$_2$ on relatively pure IrOx surface devoid of the base metal (Ir). While hydrous iridium oxide (IrOx) has been modified on boron-doped diamond by electrodeposition to study the effect of deposited quantity upon electroanalytical performance [21], insight into the electrocatalytic kinetics for H$_2$O$_2$ reduction on the Ir^{IV}Ox·nH$_2$O-electroflocculated electrode is presented in this study. Of particular emphases are characterizations of number of electrons transferred in the reaction, reaction order, potential regimes characteristic of varying rate-limiting steps, and tafel slope associated with the electrocatalytic H$_2$O$_2$ reduction, as well as amperometric detection capability evaluated under agitated and flow injection analysis (FIA) modes. The electrocatalytic mechanism of H$_2$O$_2$ reduction on the Ir^{IV}Ox·nH$_2$O electrode is also proposed.

2. Experimental

2.1. Chemicals and materials

Potassium hexachloroiridate (IV), acetaminophen (AP), hydrochloric acid, hydrogen peroxide solution, ascorbic acid (AA) were obtained from Sigma-Aldrich Corp and used as supplied. Dipotassium hydrogen phosphate, potassium dihydrogen phosphate, nitric acid, potassium chloride, sodium hydroxide were obtained from J.T. Baker. All aqueous solutions were prepared using ultrapure water (>18 MΩ cm) from a Direct-Q purification system. A glassy carbon electrode (GCE, 3 mm in diameter) purchased from Gaoss Union Inc. (Wuhan, China) was used as bare substrate to prepare the Ir^{IV}Ox·nH$_2$O nanostructured electrode. Glassy carbon and platinum rotating disk electrodes (5 mm in diameter) obtained from Pine Instrument Company (Grove city, PA) were performed in the measurements of electron transfer number, reaction order, and Tafel plot.

2.2. Preparation of Ir^{IV}Ox·nH$_2$O nanostructured electrode

Ir^{IV}Ox colloidal nanoparticles (∼2 nm) were synthesized as stated previously [44–46]. Briefly, 2.1 mM K$_2$IrCl$_6$ (15 mL) prepared in ultrapure H$_2$O was mixed with 1 mL of NaOH solution (10% w/w), which was subsequently held at 90 °C for 20 min under agitation. The resultant pH ∼ 13 solution (pale purple color) was cooled in an ice-bath for 30 min and stored at 4 °C at least 24 h before the experimental use. Electroflocculation was performed to deposit the Ir^{IV}Ox nanoparticles onto GCE in a 0.525 mM Ir^{IV}Ox colloidal solution by applying 1.3 and -0.7 V vs Ag/AgCl intermittently (1 s pulse period for each potential) for 10 min of total electroflocculation time. Prior to the electroflocculation, GCE was polished with 1, 0.3, and 0.05 μm alumina powder suspensions in sequence and rinsed with ultrapure H$_2$O thoroughly.

2.3. Electrochemical and other characterizations

Linear sweep voltammetry (LSV), cyclic voltammetry (CV), and amperometry (i-t curve) were performed in a three-electrode electrochemical cell equipped with the Ir^{IV}Ox·nH$_2$O-electroflocculated GCE working, a Pt wire auxiliary and a 3 M Ag/AgCl reference (CHI111, CH Instruments) electrodes at room temperature (∼25 °C) by using a CH Instruments 660D potentiostat. In the experiments requiring forced convection, the rotating disk GCE was used for the substrate of the working electrode and the rotation rate was controlled by a rotating electrode system (Model 616, EG&G). For the experiments under deaerated condition, dinitrogen stream was bubbled through the phosphate buffer (10 mL) at least 30 min. The potential utilized in the tafel plot was corrected based on the relationship $E = E_{app} – iR$ where E_{app} is the applied potential, R is the ohmic resistance of the electrochemical cell (50.4 ohm), i is the current recorded at the 600th s. Amount of electroactive Ir sites (Γ_{ea}) was evaluated by integrating the charge shown in the anodic peak of Ir$^{IV/III}$ redox and corrected with blank capacitive current obtained in 0.1 M phosphate buffer (pH 7.0). Coverage of Ir (Γ_{cov}) of the electroflocculated film was determined by using inductively coupled plasma mass spectrometry (Perkin-Elmer SCIEX, ELAN 6100 DRC). The Ir^{IV}Ox·nH$_2$O electrode was electrochemically anodized at 1.5 V vs Ag/AgCl in a NaOH solution (2.5 M) for more than 30 minutes to completely dissolve the deposit in the solution. No Ir$^{IV/III}$ redox peak was observed in the cyclic voltammogram given by the electrode in the solution sampled for the ICP-MS analysis.

2.4. Detection of H$_2$O$_2$

Detection of H$_2$O$_2$ was studied in both agitated and flow injection analysis (FIA) modes. Amperometric response characteristic of various H$_2$O$_2$ concentrations was recorded to generate the calibration curves. In the agitated mode, 5 μL H$_2$O$_2$ (80.2 mM) was added into 2 ml of phosphate buffer (0.1 M, pH 7.0) forming 200 μM increase in the H$_2$O$_2$ concentration. The agitation rate was 400 rpm. H$_2$O$_2$ was added at the 180th, 240th, 300th, 360th, and 420th s. The currents recorded at 239th, 299th, 359th, 419th, and 479th s were referred to as the sensing signal for corresponding levels of H$_2$O$_2$. The FIA was performed using a thin-layer fluidic cell (fluidic volume: 460 μL; fluidic thickness: 1.47 mm) (Fig. S3). The cell was made of Teflon and designed to suit the Ir^{IV}Ox·nH$_2$O-electroflocuated GCE, the Pt wire counter, and the Ag/AgCl reference electrodes in the electrolyte chamber. The carrier solution (0.1 M phosphate buffer, pH 7.0) was driven at 1 mL min^{-1} by a Gilson peristaltic pump (MINIPULS® 3). Tygon tubing (1.52 mm i.d.) was used to connect all components. Every spike contained 50 μL of H$_2$O$_2$ solution with desired concentration and was manually injected into the flowing carrier solution using a syringe at a three-way junction device. The potential applied in FIA was -0.3 V vs Ag/AgCl.

3. Results and discussion

3.1. Electrochemical characterizations of Ir^{IV}Ox·nH$_2$O

The steady-state cyclic voltammogram (50 mV/s) of the electroflocculated Ir^{IV}Ox·nH$_2$O film in 0.1 M phosphate buffer (pH 7.0) is illustrated in Fig. 1A. The Ir^{IV}Ox film undergoes two well-defined Ir-centered redox reactions, Ir$^{IV/III}$ (a_1, c_1) and Ir$^{V/IV}$ (a_2, c_2) in connection with the formal potentials ($E^{\circ\prime}$) at 0.157 and 0.512 V. The potential separation ($\Delta E = E_{pa} - E_{pc}$) of Ir$^{IV/III}$ and Ir$^{V/IV}$ redox is