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Effect of anions on the oxidation and reduction of hydrogen peroxide on the gold nanoparticle-deposited carbon fiber paper electrode

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ABSTRACT

The nanostructured gold has been shown to catalyze the oxidation of hydrogen peroxide (H_2O_2), an important analyte for clinical diagnosis. However, little is known about the effect of anions on its catalytic activity. In this study the gold nanoparticles (AuNP) of average size of 30-80 nm were electrodeposited on the carbon fiber paper (CFP) electrode to explore the effect of anions, such as phosphate, sulfate, nitrate, acetate, chloride and hydroxide ions, on the AuNP-catalyzed H_2O_2-oxidation. In phosphate solution the AuNP-deposited CFP (AuNP/CFP) exhibited high catalytic activity to H_2O_2. However, the catalytic activity of AuNP was severed blocked in solutions containing chloride, sulfate, nitrate, and acetate ions. Although hydroxide was shown to facilitate the catalysis of AuNP, the oxidation of H_2O_2 was greatly interfered by the gold oxide formation in 0.05 M NaOH. A strong dipole moment between adsorbed anions, such sulfate, nitrate and acetate, and AuNP is suggested to block the access of H_2O_2 molecules to the surface of AuNPs. This postulation is demonstrated by the finding that the electrochemical active surface area of AuNP/CFP is $0.90 \pm 0.02\ cm^2$, $0.79 \pm 0.08\ cm^2$, $0.66 \pm 0.09\ cm^2$, $0.45 \pm 0.04\ cm^2$, $0.42 \pm 0.08\ cm^2$ and $0.15 \pm 0.08\ cm^2$, in 0.05 M hydroxide, phosphate, bicarbonate, nitrate, acetate and sulfate solutions, respectively. These results indicate that the microenvironment near the surface of nanostructured Au is important to determine the catalytic activity of Au to H_2O_2.

1. Introduction

Hydrogen peroxide (H_2O_2) is an important analyte in laboratories, in health care and in food and cosmetic related industries. H_2O_2, a byproduct of bioenergetic process in organisms [1], can be used as an indication of the oxidative stress in mitochondria and cells [2,3]. In clinical diagnosis, H_2O_2 is the end product of oxidases that involved in a variety of biochemical tests and is adopted to represent the level of biochemical markers in patients [4]. In food processing, textile and cosmetic industries H_2O_2 is commonly used as disinfectant and bleach [5,6] to remove contaminates and decolorization. However, high level of residue H_2O_2 in foods or cosmetic products may cause deleterious effects, such as skin rash and irritation, nausea, vomiting, diarrhea, gastrointestinal ulcers or mucosal inflammation and even cancers. Therefore, it is essential to determine the residue H_2O_2 level in biological fluids, foods and cosmetic products to evaluate the pathophysiological status of patients and to promote safety practice in food and cosmetic industries.

Gold (Au) is an attractive electrode material for the construction of biosensors due to its high electric conductivity, good biocompatibility and high chemical stability. In addition, thiolate compounds can easily form self-assembled monolayer on Au surface. Planar Au electrode was originally known as a less active metal for catalysis [7]. However, when Au was downsized to nanometer scale, usually 5-10 nm, it exhibits a uniquely high catalytic activity to the oxidation of oxygen [8,9], carbon monoxide (CO) [10,11], alcohols [12,13], and other organic molecules [14]. Some factors have been postulated to determine the catalytic activity of Au, such as the size of Au nanoparticles (AuNPs) and the presence of reducible oxide supports, such as TiO_2, ZrO_2, NiO, Fe_2O_3 and Co_3O_4 [15,16]. However, recent studies shown that the AuNP or nanostructured Au itself could serve as the catalyst for the oxidation of reactants [9,17] as long as the significant amount of low-coordinated Au atoms or step edges [18,19] formed on the surface.

On Au disc electrode, H_2O_2 exhibited two anodic peaks in the cyclic voltammogram, one at +490 mV and another at +870 mV

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[20]. However, the first peak is more sensitive to the surface cleaning and pretreatment than the second one. The oxidation of H_2O_2 is also influenced by the pH of the solution. The peak potential of the anodic peaks shifts negatively when pH increases from 4.7 to 12. The chemisorbed hydroxide (OH^-) on Au surface was postulated to facilitate the oxidation of H_2O_2 [20]. Although the electrochemical behavior of H_2O_2 on Au disk and on nanoporous Au is studied, little is known about the effect of anions on the nanostructured Au-catalyzed oxidation of H_2O_2.

Chemisorption of oxyanions, such as OH^- [21,22], iodide (I^-) [23,24], chloride (Cl^-) [21,25], phosphate (PO_4^{3-}) [26], sulfate (SO_4^{2-}) [21,25,27], acetate (CH_3COO^-) [28], nitrate (NO_3^-) [29] and bicarbonate (HCO_3^-) [30], on Au surface was broadly studied. Among them, OH^- was shown to play a role in facilitating many redox reactions, such as the oxidation of glucose [31,32], the oxidation of H_2O_2 [20] and the reduction of oxygen [22]. The catalytic activity of Au electrode was shown to be enhanced by the modification of I^- [23,24] and inhibited by the chemisorption of Cl^- [25,32]. Although the chemisorption of other anions was postulated to perturb the overall charge and surface double-layer structure of Au electrode [25,26], their effect on the catalytic activity of Au electrode has not been reported.

In the present study the AuNP-electrodeposited carbon fiber paper (CFP) electrode was prepared and characterized. CFP, a thin two-dimensional sheet of micro-sized carbon fibers, was recently demonstrated to be a potential electrode material for the development of electrochemical biosensors due to its large surface area, high electric conductivity and stability [33,34]. Compared to bare CFP the AuNP-electrodeposited CFP (AuNP/CFP) exhibited the catalytic activity to H_2O_2. Interestingly, this catalytic activity is affected by anions. The results obtained in this study provide a guideline for the formulation of reaction solution for the determination of H_2O_2 in biological samples, when the AuNP-modified electrodes are used as the sensing electrode.

2. Materials and Methods

2.1. Materials

Carbon fiber paper (MGL190) was purchased from AvCarb. Copper foil, hydrogen peroxide (35%), tetrachloroauric (III) acid trihydrate (H_2AuCl_4), potassium hexacyanoferrate (III), sodium hydroxide, potassium sulfate, potassium bicarbonate and sodium nitrate were from Sigma. Potassium phosphate dibasic, potassium phosphate monobasic, sodium chloride, and potassium chloride were obtained from Showa. Sodium acetate was bought from Amresco. Acetic acid was obtained from Scharlau. Hydrogen chloride was from Fisher Scientific. Other regents are analytical grade.

2.2. Apparatus

The electrochemical measurements were carried out on CHI440 (CH Instruments, West Lafayette, IN, USA) by using the standard three-electrode system with the platinum as the counter electrode, the Ag/AgCl electrode as the reference electrode, and AuNP/CFP electrode as the working electrode. Oxygen plasma treatment was done on the Plasma Cleaner (Model: Zepto, Diener electronic, Ebhausen, Germany). Scanning electron microscope (SEM) images and energy-dispersive X-ray (EDX) spectroscopy analysis were carried out on the S-4700, Type II+ Horiba, EMAX-ENERGY EX-300 (Hitachi, Japan).

2.3. Preparation of AuNP/CFP electrode

The CFP-based working electrodes with a working area of $0.3 \times 0.5\,cm^2$ were prepared as described previously [34]. The plasma treatment was performed in the reaction tube of the plasma cleaner under the pressure of <0.4 mbar and oxygen flow rate of 40 N/h, at 75 watts for 15 s. Different concentrations of H_2AuCl_4 (0.13, 0.33, 0.65, 1.3, 2.6 mM) was prepared by dissolving in 0.01 M phosphate buffer at pH 8.0. The electrodesposition of AuNPs on plasma-treated CFP was carried out by cyclic voltammetry (CV). The CV was performed over the potential range between -0.4 V and -1.3 V at a scan rate of 50 mVs^{-1} for 20 consecutive cycles.

2.4. Electrochemical measurement

The stock anion solutions, including NaCl, KCl, NaOH, $NaCH_3CO_2$, K_2HPO_4, K_2SO_4, KHCO3, $NaNO_3$ and HCl, were prepared in double-deionized water. Cyclic voltammetry of the developed electrodes were carried out in different anion solutions within various potential ranges as indicated in each experiment. The working potential was maintained at +0.32 V vs. Ag/AgCl or specified in each experiment for the chronopotentiometric measurement of H_2O_2.

2.5. Estimation of heterogeneous electron transfer rate constant

The heterogeneous electron transfer rate constant (k^0) of CFP electrode with and without AuNP-coating could be estimated using the equation $\Psi = k^0\,[\pi D n \nu F/(RT)]^{-1/2}$ [35,36]. Where, k^0, n, ν, F, R and T are the heterogeneous electron transfer rate constant of an uncomplicated quasi-reversible electrochemical reaction, the electron transfer number, the scan rate ($V\,s^{-1}$), the Faraday constant, the gas constant and absolute temperature (298 K), respectively. The diffusion coefficient (D) used is $4.24 \times 10^{-6}\,cm^2\,s^{-1}$ [24] for hexacyanoferrate (III). Ψ was derived using the empirical equation: $\Psi = (-0.6288 + 0.0021X)/(1 - 0.017X)$, [36]. X is ΔEp expressed in mV. The k^0 was then calculated from the slope of the plot of Ψ vs. $[\pi DnF/(RT)]^{-1/2}\nu^{-1/2}$.

3. Results and Discussion

3.1. Preparation and characterization of AuNP/CFP electrode

Electrodeposition of nanostructured Au on plasma-treated CFP was done by CV in various concentrations of H_2AuCl_4 solution. After electrodeposition, the electrochemical behavior of AuNP/CFP was analyzed by CV in 0.05 M phosphate buffer, pH 8.0 in the potential range between +0.0 V and +1.2 V. An anodic peak at +0.87 V and a cathodic peak at +0.46 V corresponding to Au oxidation [22] and the reduction of Au oxide [22,31,32], respectively, could be seen in the cyclic voltammogram of AuNP/CFP (Fig. 1A). In the presence of 0.5 mM H_2O_2, a new anodic peak appeared at +0.40 V (Fig. 1B), which was unseen in CFP only (Fig. 4). Both Au redox peaks and H_2O_2 oxidation peak increased when AuNP/CFP electrodes were prepared with H_2AuCl_4 concentrations increased from 0.13 to 2.60 mM. The best performance of the prepared AuNP/CFP electrode was justified by the balance between the oxidation of H_2O_2 (at +0.40 V), which should be as high as possible, and Au oxidation (at +0.87 V), which should be as low as possible. Hence, the 1.3 mM $HAuCl_4$ solution was chosen as the optimal concentration for the preparation of AuNP/CFP. The optimization of electrodeposition of AuNPs was further performed by running CV consecutively in 1.3 mM $HAuCl_4$ solution from 5 to 40 cycles. As shown in Fig. S1A (Supplementary results), the AuNP/CFP prepared with 20 consecutive cycles of CV exhibited the best performance (Fig. S1B, Supplementary results). Therefore, in the following experiments the AuNP/CFP electrodes were prepared on plasma-treated CFP by 20 consecutive cycles of CV in the potential range of -0.4 V and -1.3 V and at the scan rate of