Research Article

Electrocatalytic Oxidation of Hydrogen Peroxide Based on the Shuttlelike Nano-CuO-Modified Electrode

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Received 12 August 2011; Revised 20 October 2011; Accepted 20 October 2011

Academic Editor: Suna Timur

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CuO nanocrystals were prepared with hydrothermal synthesis method. The morphology of the nano-CuO was characterized by scanning electron microscopy. The prepared shuttlelike CuO nanocrystals were modified to glass carbon electrode (GCE) to form nano-CuO/GCE modified electrode. The obtained modified electrode showed an excellent electrocatalytic property towards hydrogen peroxide in 0.01 M NaOH containing 0.09 M KCl electrolyte. Under the optimal experiment conditions, the electrocatalytic response current of this sensor was proportional to the H$_2$O$_2$ concentration in the range of 0.02 μM $\sim$ 250 μM with a detection limit down to 7 nM (signal/noise = 3). The sensitivity was calculated to be 227 μA/mM. The H$_2$O$_2$ sensor exhibited low detection limit, fast response time, and good reproducibility and could be applied to determine hydrogen peroxide.

1. Introduction

Among numerous biological, chemical, environmental, pharmaceutical, and clinical studies, hydrogen peroxide plays a fundamental role as an oxidizing, bleaching and sterilizing agent [1]. There are a variety of methods with respect to development for the detection of hydrogen peroxide, such as spectrophotometry [2, 3], fluorimetry [4], chromatography [5, 6], chemiluminescence [7, 8], and titrimetry [9]. Compared with these methods, electrochemical techniques have inherent advantages of simplicity, ease of miniaturization, high sensitivity, and relatively low cost and could be applied to determine H$_2$O$_2$ [10, 11]. Because of slow electrode kinetics and high overpotential during redox reaction [12], it was usually difficult to test H$_2$O$_2$ with a conventional electrode. Here, the preparation of chemically modifying electrode with catalytic effect was of valuable significance. Pournaghi-Azar et al. [13] have described the non-electrolysis preparation path of the PB films on the Al surface covered by metallic palladium particles (Pd/Al) with the two-step chemical modification and studied the electrochemical behavior of H$_2$O$_2$ reduction on the PB/Pd–Al electrode as an improved electrocatalyst. This sensor exhibited good characteristics via improved stability and electrocatalytic activity. Kumar and Chen [14] prepared poly (p-aminobenzene sulfonic acid-) (PABS-) modified glassy carbon electrode via the electrochemical deposition, PABS was strongly and irreversibly adsorbed onto GC electrode surface, and the PABS-modified electrode was successfully utilized as an enzyme-less amperometric sensor for detection of H$_2$O$_2$. The sensor showed potent electrocatalytic activities and improved electron transfer abilities.

Nanoparticles as modification materials have been extensively employed in various fields owing to the small size, large surface area, and some other especial properties. Numerous nanometal oxides, such as manganese dioxide [15], nickel oxide [16], zinc oxide [17], and cobalt oxide [18], have attracted considerable interest in the analytical area. Among those nanoparticles, nano-CuO has earned more and more interests thanks to its distinctive properties [19, 20], such as high stability and good electrical properties. Different synthetic methods have been studied for the preparation of CuO nanoparticles with various morphologies, including nanowire, nanosheet, nanorod, and nanoflower. McAuley et al. [21] synthesised CuO nanorod agglomerates and prepared the nano-CuO-modified electrode by dropping it onto the electrode. The electrochemical behavior of hydrogen peroxide on the nano-CuO-modified electrode was studied and a limit of detection of 0.22 μM was obtained. Song et al. [22] reported that the CuO nanoflower film could be directly
2. Experimental

2.1. Reagent and Materials. Hydrogen peroxide (30% (v/v) aqueous solution) was purchased from Sinopharm Chemical Reagent Co., Ltd. The stock solutions were prepared fresh with doubly distilled water. All other reagents were purchased from Shanghai Chemical Reagent Company and were of analytical grade and used without further purification. Doubly distilled water was used throughout the experiments. The supporting electrolyte we used in this experiment was 0.1 M NaOH solution containing 0.09 M KCl.

2.2. Apparatus and Measurements. All the electrochemical measurements including cyclic voltammetry (CV) and amperometric response (i-t) were carried out with CHI660A electrochemical workstation (Chenhua Instruments Co., Shanghai, China). A conventional three-electrode system was employed. A bare glass carbon electrode (GCE, Ø3.0 mm) or nano-CuO-modified GCE was used as the working electrode, and an Ag/AgCl (KCl, 3.0 M) electrode and a platinum wire electrode were used as the reference electrode and the counter electrode, respectively. A magnetic stirrer provided the convective transport during the amperometric measurements. All experiments were performed at room temperature. Scanning electron microscopy (SEM) was obtained on S-4800 field emission scanning electron microanalyzer (Hitachi, Japan).

2.3. Preparation of the Nano-CuO-Modified Electrodes. The preparation of the nano-CuO was performed as follows: in the first place, 0.25 g Cu(CH$_3$COO)$_2$·H$_2$O and 0.77 g cetyltrimethylammonium bromide (CTAB) were put in a 60 mL teflon-lined stainless steel autoclave, then 40 mL doubly distilled water was poured into the autoclave with stirring. Afterward, 4 mL, 0.5 M NaOH was tardily added into the above solution under stirring. Completing all the above steps, it was necessary to make sure that the autoclave was tightly sealed. Meanwhile, the temperature of autoclave was maintained at 120 °C for 12 h and then cooled to room temperature naturally. The precipitate was centrifuged and washed with doubly distilled water and absolute ethanol several times over and over, then dried in vacuum at 70 °C for several hours.

Prior to the modification, the GCE was mechanically polished with alumina powder (Al$_2$O$_3$, 0.05 μm) up to a mirror-like, then cleaned by ultrasonication in water and ethanol, and then rinsed with doubly distilled water and dried. A nano-CuO dispersion solution (0.8 mg mL$^{-1}$) was prepared with dispersing ultrasonication nano-CuO particle into doubly distilled water. A certain volume dispersion solution was dropped onto surface of a clean GCE, and then electrode was dried for 30 minters under room temperature to evaporate solvent, leaving the nano-CuO particle immobilized onto the surface of electrode.

3. Results and Discussion

3.1. Surface Characterizations. Via scanning electron microscopy (SEM), the morphologies and structures of the surface film of the modified electrode was characterized. Figure 1 shows scanning electron microscopy image of nano-CuO film. From the figure, the shuttlelike nano-CuO was evenly distributed on surface of electrode. The CuO nanocrystals looked like shuttles; furthermore, the sizes were similar and the distribution was also average on the whole. And the nano-CuO nanocrystals took on large specific surface area. A Nyquist diagram of electrochemical impedance spectrum was an effective way to measure the electron-transfer resistance. Figure 2 shows electrochemical impedance spectra of bare GCE and nano-CuO/GCE in 1 M KCl in the presence of 1 mM [Fe(CN)$_6$]$^{3−/4−}$ as the redox probe. As seen in Figure 2, curve a was a Nyquist plot of a bare GCE in 1 mM [Fe(CN)$_6$]$^{3−/4−}$. It exhibited an almost straight line, which implied an extremely low electron-transfer resistance.
to the redox probe. After a modification with nano-CuO film, the electron-transfer resistance reached a higher value and the interfacial $R_e$ increased, which was due to the impediment of electron transfer in the presence of the nano-CuO film. It indicated that the CuO shuttlelike nanocrystals were immobilized on the GCE successfully.

3.2. Electrochemical Characteristics of the Sensor. The electrochemical behaviors of H$_2$O$_2$ on nano-CuO/GCE were explored. As shown in Figure 3(a), there was no electrochemical response to H$_2$O$_2$ on the bare GCE in 0.01 M NaOH + 0.09 M KCl solution. However, there was a large anodic peak of H$_2$O$_2$ on the nano-CuO/GCE under the same experimental condition, and the potential of anodic peak was at 0.19 V. For comparison, the cyclic voltammetric experiment was performed with nano-CuO/GCE in 0.01 M NaOH + 0.09 M KCl solution not containing H$_2$O$_2$. There was no obvious redox peak on CV curves between the given potential range (figure, not shown). A large anodic peak indicated that H$_2$O$_2$ could yield redox reaction on the nano-CuO/GCE. Probable mechanisms could be suggested to explain the anodic oxidation of H$_2$O$_2$ in alkaline medium:

$$\text{H}_2\text{O}_2 + 2\text{OH}^- - 2e \rightarrow 2\text{H}_2\text{O} + \text{O}_2.$$  \hfill (1)

The dependence of H$_2$O$_2$ anodic peak current on scan rates was examined. Figure 4 showed the cyclic voltammograms of H$_2$O$_2$ on the nano-CuO film in 0.01 M NaOH + 0.09 M KCl containing 0.1 mM H$_2$O$_2$ solution. The experimental result indicated that the anodic peak current of H$_2$O$_2$ ($I_{pa}/\mu$A) was proportional to the square root of scan rate ($\nu/Vs^{-1}$) ($I_{pa} = -74.05\nu^{1/2} - 1.15, R^2 = 0.999$), suggesting that the electrode process was controlled by diffusion as expected for a catalytic system.

3.3. Optimization of the Experiment Conditions. In order to optimize the electrocatalytic response to H$_2$O$_2$ on the nano-CuO/GCE, the effect of NaOH concentration and the nano-CuO film thickness on anodic peak current was explored. Maintaining system ion concentration 0.1 M, the concentrations were changed from 0.001 to 0.1 M for NaOH and from 0.099 to 0 for KCl. With increment of NaOH concentration, anodic peak current of H$_2$O$_2$ increased. When NaOH concentration was improved to be 0.01 M, the peak current achieved the best value. Subsequently, it came to a gradual decrease with increasing NaOH concentration. Accordingly, during this experiment we chose 0.01 M NaOH containing 0.09 M KCl as the supporting electrolyte.

In preparing the sensor, the amount of modifying material on the surface of electrode influences the sensor response to detecting target. Hence, the influence of nano-CuO film thickness on electrode on sensor response to H$_2$O$_2$ was examined in this paper. The amount of nano-CuO on the GCE was controlled to be 0.028, 0.056, 0.085, 0.113, 0.142,
and 0.212 mg (cm$^{-2}$), respectively, and the anodic peak currents of 0.1 mM H$_2$O$_2$ were measured. The experimental results showed that anodic peak current of H$_2$O$_2$ increased with the increment of the nano-CuO amount. When the amount of nano-CuO was improved to be 0.113 mg (cm$^{-2}$), the peak current achieved the best value. Subsequently, it came to a gradual decrease with increasing the nano-CuO amount (shown in Figure 5). With increasing the amount of nano-CuO on surface of electrode, the electrocatalytic active area increased, and it also promoted electron transfer in the redox of H$_2$O$_2$. When the amount of nano-CuO was in excess of 0.113 mg (cm$^{-2}$), the conductivity of modified electrode decreased and the anodic peak current of H$_2$O$_2$ decreased.

3.4. Amperometric Response to H$_2$O$_2$ and the Calibration Curve. The amperometric response of nano-CuO/GCE upon adding H$_2$O$_2$ little by little every 50 s was tested at the applied potential 0.19 V in 0.01 M NaOH containing 0.09 M KCl electrolyte solution with continuous stirring under the optimal conditions. As shown in Figure 6(a), good responses were observed during the successive addition of 2, 6, and 20 μM H$_2$O$_2$, respectively. The response of preparing sensor to low-concentration H$_2$O$_2$ was shown in Figure 6 (inset b), which demonstrated an effective catalytic property of nano-CuO material. It could be observed that the response current was linear with H$_2$O$_2$ concentration in the range from 0.02 to 250 μM. The regression equation was $Y (\mu A) = -1.69 - 0.227X (\mu M)$ with the correlation coefficient being 0.995, and the detection limit was computed to be 7 nM (S/N = 3) at a signal-to-noise ratio of 3. The sensitivity was calculated as 227 μA mM$^{-1}$. Such high sensitivity could be attributed to the fact that high-density CuO shuttlelike nanostructure can greatly increase the electrocatalytic active area and also promote electron transfer in the redox of H$_2$O$_2$ [22]. Table 1 summarized the dissimilar performance of the H$_2$O$_2$ sensors based on different-materials-modified electrodes.

The stability and reproducibility of this sensor were also examined. The prepared electrochemical sensor possessed long-term stability because the nano-CuO material could strongly be adsorbed on surface of glassy carbon electrode. We used this electrochemical sensor to detect H$_2$O$_2$ several times every day intermittently and also studied the storage stability of the sensor by storing it in air at ambient conditions when not in use. Three days later the response of the sensor maintained 99.2% and after three weeks the response retained 93.6% of the original value. This study indicated that nano-CuO/GCE have good stability and it can be used repeatedly.

<table>
<thead>
<tr>
<th>Material</th>
<th>Linear range (μM)</th>
<th>Detection limit (nM)</th>
<th>Sensitivity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT/Ag nanohybrids</td>
<td>50~17000</td>
<td>500</td>
<td>1.42 μA mM$^{-1}$</td>
<td>[24]</td>
</tr>
<tr>
<td>Nano-TiO$_2$/DNA/thionin nanocomposite</td>
<td>50~22300</td>
<td>50000</td>
<td>—</td>
<td>[15]</td>
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<tr>
<td>Nafion and copper oxide nanoparticles</td>
<td>0.15~9000</td>
<td>60</td>
<td>—</td>
<td>[10]</td>
</tr>
<tr>
<td>CuO flower-like nanomaterials</td>
<td>42.5~4000</td>
<td>167</td>
<td>88.4 μA mM$^{-1}$ cm$^{-1}$</td>
<td>[22]</td>
</tr>
<tr>
<td>CuO shuttlelike nanocrystals</td>
<td>0.02~250</td>
<td>7</td>
<td>227 μA mM$^{-1}$</td>
<td>This study</td>
</tr>
</tbody>
</table>

![Figure 5: Current response of nano-CuO/GCE for 0.1 mM H$_2$O$_2$ inside the electrochemical reactor at various modification amounts of nano-CuO on the electrode, electrolyte: 0.01 M NaOH + 0.09 M KCl solution.](image)

![Figure 6: Amperometric current-time curves for H$_2$O$_2$ oxidation on the nano-CuO/GCE, at applied potential 0.19 V (versus Ag/AgCl) in 0.01 M NaOH + 0.09 M KCl solution. Concentrations were used in the range between 0.02 μM and 250 μM H$_2$O$_2$. (a) the current-time curves for adding 0.02, 0.06, and 0.2 μM of H$_2$O$_2$, (b) the current-time curves for adding 2, 6, and 20 μM of H$_2$O$_2$. (c) showed $I_{pa}$ versus $C_{H_2O_2}$.](image)
area and also obviously promote electron transfer abilities between H$_2$O$_2$ molecules and electrode. The nano-CuO/GCE exhibited the prominent activity for redox of H$_2$O$_2$, and the fabricated sensor gave a good stability and reproducibility, which could be used as an amperometric sensor for determination of low-concentration H$_2$O$_2$ in samples.

### Acknowledgments

The authors thank the National Natural Science Foundation of China (Grant no. 20775002) for financial support. The paper was supported by Program for Innovative Research Team in Anhui Normal University.

### References


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