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Sensitive Electrochemical Determination of Hydrogen Peroxide Using Copper Nanoparticles in a Polyaniline Film on a Glassy Carbon Electrode

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ABSTRACT

Rapid and accurate determination of hydrogen peroxide is necessary in biochemistry and environmental science. In this paper, a sensitive hydrogen peroxide electrochemical sensor was developed by cyclic voltammetry deposition of polyaniline–copper nanocomposite film on a glassy carbon electrode. The synthesized polyaniline/Cu composites were characterized by scanning electron microscopy and X-ray diffraction. With a typical working potential of 0.4 V (versus Ag/AgCl) and a pH value of 6.0, the prepared electrochemical sensor achieved linear range of 1.0–500 μM for hydrogen peroxide detection. A relative standard deviation of 4.9% for $n = 7$ and 10.0 μM of H_2O_2 and a limit of detection of 0.33 μM at a signal-to-noise ratio = 3 were observed. The sensor was successfully used for the analysis of tap water, and a spiked recovery of $93.0 \pm 2.1\%$ was obtained, further confirming the sensor's accuracy and feasibility.

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Cyclic voltammetry; glassy carbon electrode; hydrogen peroxide; scanning electron microscopy; X-ray diffraction

Introduction

Hydrogen peroxide (H_2O_2) is a distinctive oxidant and has been widely applied in wastewater treatment, pharmaceutical, mining, textile, paper, food manufacturing, and chemical industries (Ramachandran et al. 2016). H_2O_2 existing in the atmosphere and the natural water supply could promote the formation of H_2SO_4 and HNO_3 , which may increase the acidity of rain and decrease the pH of waterways (Hug and Leupin 2003; Ciardelli, Xu, and Sahai 2008). It is also an important by-product of oxidases in living organisms (Giorgio et al. 2007) which acts as an oxidative stress marker, signaling molecule, and defense agent in biochemical reactions (Yuan et al. 2012; Chen et al. 2016). Recently, researchers have observed that exposure to H_2O_2 could lead to Parkinson's, Alzheimer's, cancer, and diabetes as well as cardiovascular and neurodegenerative disorders (Miller, Dickinson, and Chang 2010; Xie et al. 2016). In addition, the ingestion of H_2O_2 through drinking water may cause headaches, nausea, dizziness, and vomiting in humans. Therefore, the development of techniques and tools for

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accurately monitoring the concentration of H_2O_2 has attracted great attention (Xiao, Ju, and Chen 1999).

To date, a series of techniques have been developed for detecting H_2O_2 , such as titrimetry (Klassen, Marchington, and McGowan 1994), spectrometry (Yan, Tao, and Toghiani 2009), chemiluminescence (Xu et al. 2016), and electrochemistry (Wang and Gu 2009). Compared with these methods, electrochemical methods have gained wide attention due to their high sensitivity, simple operation, rapid process, and low cost (Wang et al. 2013). In general, most electrochemical techniques use immobilized enzymes such as horseradish peroxidase (Xu et al. 2015), cytochrome (Oszajca et al. 2016), or hemoglobin (de Albuquerque et al. 2016) to construct electrochemical biosensors. These enzyme-based detection methodologies are often unstable, expensive, and time-consuming. To improve these sensors, modification of the electrode with different nanoparticles has been investigated as an alternative to enzyme immobilization on the electrode surface (Zhang et al. 2008; Song, Hwang, and Whang 2010; Liu, Liu, and Chen 2013).

Copper nanoparticles have been successfully used to improve the electrode performance in detecting H_2O_2 because of the low cost, good electrochemical activity, and biocompatibility (Dong et al. 2016; Deyasenathipathy et al. 2016). In recent years, various synthetic methods for the preparation of Cu nanoparticles including hydrothermal, chemical, electrochemical, sonochemical, microirradiation, and ultraviolet irradiation have been developed. Electrochemical methods with the advantages of simplicity and low cost have shown a promising future for preparation of Cu nanoparticles with high purity and uniformity. To date, electrochemical sensors based on Cu nanoparticles in polyaniline film have been rarely reported. For example, Selvaraju and Ramaraj (2009) reported early the electrocatalytic activity of Cu nanoparticles on a glassy carbon electrode for the reduction of H_2O_2 . Nanowire–Cu nanocomposite has also been introduced in a nonenzymatic H_2O_2 sensor simultaneously by combining with polypyrrole film (Meng et al. 2013). Recently, an effective H_2O_2 sensors using Cu–Ni nanoparticles decorated on nitrogen-doped graphene nanocomposite has been reported by Shabnam et al. (2017). As excellent conducting polymers, the usage of polyaniline in these H_2O_2 sensors involving Cu nanostructures is still rare and it is expected to an important enhancing medium.

In this paper, we synthesized Cu nanoparticles using electrodeposition methods and then fixed these metallic nanoparticles on the surface of an electrode by conductive polymer films to improve their electrochemical performance. A novel nonenzyme H_2O_2 sensor based on Cu nanoparticles incorporated into polyaniline film was developed. The electrocatalytic activities of the prepared electrode toward H_2O_2 have been studied, and its performances in the analysis of tap water have also been evaluated.

Experimental

Reagents and instruments

All chemicals used were of at least analytical reagent grade. Deionized water ($18.2 \text{ M}\Omega \cdot \text{cm}$, obtained from a Milli-Q purification system, Billerica, USA) was used for standard reagents and sample dilutions. Aniline, sulfuric acid (98%), and H_2O_2 (30%) were purchased from Sinopharm Chemical Reagent (Shanghai, China). Phosphate-buffered saline with different pH values were prepared from 0.1 M K_2HPO_4 and 0.1 M NaH_2PO_4 stock solution. The water samples (tap water) were obtained in our lab (CAS Key Laboratory of Biobased

Materials). The samples were passed through a 0.22- μm filter to remove impurities. All solutions were deaerated with high-purity argon gas for at least 10 min before any electrochemical measurements.

All electrochemical experiments were performed using a CHI 660E workstation (Shanghai Chenhua Instrument, China) with a three-electrode system consisting of a working electrode (bare glassy carbon electrode or modified electrodes, $\Phi = 4.0$ mm), an auxiliary platinum electrode, and an Ag/AgCl (sat. KCl) reference electrode. Scanning electron microscope images were obtained using a Hitachi S-4800 field emission instrument (Hitachi, Japan). X-ray diffraction analysis of the samples was performed using a D8 Advance, Bruker. Indium tin oxide electrodes were purchased from Xiang Science and Technology with resistance value of $8\ \Omega\ \text{cm}^{-2}$.

Preparation of modified electrodes

Before modification, the glassy carbon electrode was polished with a 0.05- μm alumina slurry. Next, the electrodes were sonicated in acetone, ethanol, and deionized water for approximately 5 min. The electrode was then modified through the electrosynthesis of a polyaniline film on its surface in 0.5 M H_2SO_4 containing 0.1 M aniline as the electrolyte (Li et al. 2014). The potential range of the working electrode was swept between -0.2 and 0.8 V versus Ag/AgCl (in saturated KCl) for the first five cycles, and between -0.2 and 0.75 V for the next three cycles to prepare the polyaniline film to avoid its overoxidation (Wang et al. 2011; Chani et al. 2013). The polyaniline film-modified glassy carbon electrode was washed with deionized water and dried under argon (denoted as the polyaniline electrode) for subsequent modification. The Cu nanoparticles were electrodeposited on the polyaniline electrode surface by cycling the potential from 0.0 to 1.1 V in $1\ \text{mM}$ CuSO_4 and H_2SO_4 solution with a scan rate of $50\ \text{mV s}^{-1}$ 10 times (Ulubay and Dursun 2010). The electrode was washed with deionized water and dried under argon (denoted as the polyaniline/Cu electrode) before any H_2O_2 detection. Similarly, a Cu nanoparticle-modified glassy carbon electrode (Cu electrode) was prepared without the polyaniline film.

Results and discussion

Characterization of the polyaniline and Cu nanoparticles

Typical scanning electron microscopy images of the polyaniline film and polyaniline/Cu are shown in Figure 1. To facilitate the tests, the products were synthesized on the surface of indium tin oxide electrodes. The surface of polyaniline was relatively flat (Figure 1a) with no wrinkles or small particles. When Cu nanoparticles were synthesized on the polyaniline film (Figure 1b), some wrinkles and small particles appeared on the surface.

The X-ray diffraction patterns for the resultant nanoparticles are shown in Figure 2. For the Cu nanoparticles (Kim et al. 2006), three sharp crystalline peaks at 2θ values of 39.1° , 53.0° , and 61.4° which are consistent with the (1 1 1), (2 2 0), and (3 1 1) diffraction planes of Cu nanoparticles (JCPDS, copper file number 04-0836). The typical X-ray diffraction spectrum for the synthesized polyaniline film displayed a diffuse broad peak at 2θ ranging from 20° to 26° corresponded to (1 1 1) and (2 0 0) planes (Zhang et al. 2016). The polyaniline/Cu nanoparticles have almost all the characteristic peaks of Cu and polyaniline, confirming that Cu nanoparticles have been loaded on the surface of polyaniline.

Figure 1. Scanning electron microscopy images of (a) polyaniline ($\times 4030$) and (b) polyaniline/Cu ($\times 3500$) composite nanoparticles.

The Fourier transform infrared spectrum of polyaniline and polyaniline/Cu is shown in Figure S1. Both samples presented the characteristic peaks of polyaniline (Qiu et al. 2017) with higher absorption in polyaniline films than in polyaniline/Cu films. The bands appearing at 1592 and 1396 cm^{-1} correspond to $\text{C}=\text{N}$ and $\text{C}=\text{C}$ stretching mode from the quinoid and benzenoid rings, respectively. The aromatic ($\text{C}-\text{N}$) stretching bands appearing at 1257 and 786 cm^{-1} are in agreement with the $\text{C}-\text{H}$ out-of-plane bending vibration. The band at 1070 cm^{-1} is assigned to the vibrational modes of $-\text{NH}-$ structure. These characteristic peaks of polyaniline in polyaniline/Cu composite nanoparticles indicated the formation on the surface of the electrode.

Electrocatalytic performance of the polyaniline/Cu electrodes

To distinguish the effects of modified components, the electrocatalytic behavior of glassy carbon electrode, Cu electrode, polyaniline electrode, and polyaniline/Cu electrode toward H_2O_2 was explored using cyclic voltammetry. For the bare glassy carbon electrode, there were no obvious oxidation or reduction peaks (Figure 3). For the Cu electrode, it shows

Figure 2. X-ray diffraction pattern of (a) polyaniline/Cu nanocomposites and (b) Cu nanoparticles.

Figure 3. Cyclic voltammograms of bare glassy carbon electrode in the (a) absence and (b) presence of $10\ \mu\text{M}$ H_2O_2 in $0.1\ \text{M}$ phosphate buffer (pH 6.0) at a scan rate of $0.1\ \text{V s}^{-1}$.

a redox peak at $-0.04/-0.12\ \text{V}$ (Figure 4), corresponding to the redox couples of Cu(II)/Cu(0) . With the H_2O_2 addition, the irreversible H_2O_2 reduction leads to an obvious current increase starting at about $-0.40\ \text{V}$ in the Cu electrode system. For polyaniline electrode, there was an oxidation peak at approximately $0.08\ \text{V}$ (Figure 5) and an obvious reduction peak at approximately $0.02\ \text{V}$, which correspond to the oxidation and reduction of aniline, respectively. This result also confirmed the successful modification of polyaniline film and Cu nanoparticles on the surface of electrode. When the two electrocatalysts were integrated with each other (Figure 6), the cathodic current resulted from H_2O_2 oxidation starting at about $-0.40\ \text{V}$ increases dramatically. The current increment at about $-0.4\ \text{V}$ can reach up to $22\ \mu\text{A}$. Compared with bare electrode, polyaniline electrode, and Cu electrode, the increased currents of polyaniline/Cu electrode indicated that conductive polyaniline film and Cu nanoparticles might enhance the electrode's electrocatalytic response to H_2O_2 .

Figure 4. Cyclic voltammograms of the Cu electrode in the (a) absence and (b) presence of $0.1\ \text{mM}$ H_2O_2 in $0.1\ \text{M}$ phosphate buffer at pH 6.0 and a scan rate of $0.1\ \text{V s}^{-1}$.

Figure 5. Cyclic voltammograms of polyaniline electrode in the (a) absence and (b) presence of 0.1 mM H_2O_2 in 0.1 M phosphate buffer at pH 6.0 and a scan rate of 0.1 V s^{-1} .

To evaluate the synergistic effects of polyaniline film and Cu nanoparticles, amperometric current–time curves were also studied. In a typical process, the amperometric responses with different electrodes were recorded separately after successively adding $10 \mu\text{M}$ H_2O_2 in phosphate-buffered saline (pH = 6.0) at a constant potential of -0.4 V for each electrode (Figure 7). There was no significant electrocatalytic current of the bare electrode (Figure 7a) and polyaniline electrode (Figure 7b). Moreover, the cathodic peak current increased at the Cu electrode (Figure 7c). Compared with other electrodes, the polyaniline/Cu electrode (Figure 7d) exhibited excellent response, which meant that polyaniline has a wide surface area and the copper nanoparticles were attached to these sites. Thus, the polyaniline/Cu electrode may be used for the sensitive detection of H_2O_2 .

Figure 6. Cyclic voltammograms of polyaniline/Cu electrode in the (a) absence and (b) presence of 0.1 mM H_2O_2 in 0.1 M phosphate buffer at pH 6.0 and scan rate of 0.1 V s^{-1} .

Figure 7. Amperometric determination of different electrodes with $10.0 \mu\text{M}$ H_2O_2 added successively in the electrolyte: (a) bare glassy carbon electrode; (b) polyaniline electrode; (c) Cu electrode; and (d) polyaniline/Cu electrode at $\text{pH} = 6.0$ and an applied potential of -0.4 V .

Effects of pH, applied potential, and scan rate

In general, the pH of electrolyte and applied potentials are essential parameters to the electrocatalytic process of an electrochemical sensor. In this study, their effects were studied, and the results are shown in Figures 8 and 9. The greatest cathodic peak currents with good shape and low background were obtained at $\text{pH} 6.0$; therefore, this was selected as the working pH value. At this pH value, -0.4 V was investigated as the optimal applied potential in the range of -0.6 – 0 V . In all subsequent experiments, these conditions were used.

The effects of scan rate on the cyclic voltammograms in polyaniline electrode and polyaniline/Cu electrode systems are shown in Figure S2. The reduction peak currents at -400 mV correspondingly increased with increased scan rates with a direct proportionality between them. These results indicate that the electron transfer process for H_2O_2 at the polyaniline/Cu electrode was controlled by surface-confined effects.

Figure 8. Effect of potential on the polyaniline/Cu-modified electrode in 0.1 mM H_2O_2 at $\text{pH} = 6.0$.

Figure 9. Effect of the pH on the polyaniline/Cu-modified electrode in 0.1 mM H₂O₂ at an applied potential of −0.4 V.

Performance of polyaniline/Cu electrode for determining H₂O₂

Under the optimized experimental conditions, the typical current–time responses of H₂O₂ were studied to evaluate the performance of polyaniline/Cu electrode. With specific concentrations of H₂O₂ being sequentially added into the electrolyte, the reduction currents increased linearly. Between 1.0 and 500 μM H₂O₂, the linear relationship may be expressed with the regression equation: $\Delta I(\mu A) = -0.0183c(\mu M) - 0.0806$, with a coefficient of determination (R^2) of 0.9992 and a limit of detection of 0.33 μM based on a signal-to-noise ratio of 3.

As summarized in Table 1, compared with some other nonenzymatic H₂O₂ sensors reported previously, the proposed method presents competitive analytical performance. The limit of detection (0.33 μM) is at least at the same level as the previous methods except for the Cu₂O/Nafion/gold electrode. In addition, the linear ranges (1.0 to 500 μM) in our study cover a wider range than most reported electrochemical methods. The sensitivity and

Table 1. Comparison of electrochemical methods for detecting H₂O₂.

Sensor	Linear range (μM)	Limit of detection (μM)	Reference
Polypyrrole/Cu/gold electrodes	7–4300	2.3	Liu, Liu, and Chen (2013)
CuO/copper foil	42.5–40,000	0.167	Song, Hwang, and Whang (2010)
Cu ₂ O/graphene/glassy carbon electrode	300–7800	20.8	Zhang et al. (2008)
Cu/CuO/glassy carbon electrode	3–8000	210	Deyasenathipathy et al. (2016)
Carbon quantum dots/Cu ₂ O/nafion/glassy carbon electrode	5–5300	2.8	Dong et al. (2016)
Pt/polyaniline/mesoporous silica/indium tin oxide electrode	1–2000	0.24	Li et al. (2014)
Polyaniline/multiwalled carbon nanotubes/Au/gold electrode	3–600	0.3	Narang, Chauhan, and Pundir et al. (2011)
Cu ₂ O/nafion/gold electrode	0.25–5000	0.06	Yan et al. (2013)
Polyaniline/Cu/glassy carbon electrode	1.0–500	0.33	This work

linear range indicate the great potential for the practical application of polyaniline/Cu electrode for detecting H_2O_2 .

One millimolar glucose, ascorbic acid, KNO_3 , FeCl_3 , CuCl_2 , ZnCl_2 , CaCl_2 , BaCl_2 , and NaCl presented almost no interferences for the polyaniline/Cu electrode detecting H_2O_2 (Figure S3), suggesting that polyaniline/Cu electrode could handle solutions with these common interference species without problems. The reproducibility of polyaniline/Cu electrode was evaluated under the same experimental conditions ($10.0\ \mu\text{M}$ H_2O_2 in phosphate buffered saline solution) and a relative standard deviation ($n = 7$) of 4.9% was achieved. The stability of polyaniline/Cu electrode was evaluated under optimum conditions after storage in a refrigerator for 7 and 30 days. The current responses in $10.0\ \mu\text{M}$ H_2O_2 solutions were 95.4 and 93.2% of the original current, respectively. Thus, the prepared polyaniline/Cu electrode gives reproducible results and is stable for detecting H_2O_2 .

Sample analysis

The prepared electrode was used for the analysis of tap water. Under the optimized experimental conditions, $100.0\ \mu\text{L}$ of tap water and varied amounts of a standard H_2O_2 solution were added into $10.0\ \text{mL}$ of electrolyte. The current signals were recorded to evaluate the application potential of polyaniline/Cu electrode (Figure S4). The tap water samples contain H_2O_2 itself and the concentration is not in our linear range. The results of H_2O_2 concentration are calculated from the calibration curve in real samples. In the three parallel spiked tap water samples, $1.69 \pm 0.15\ \mu\text{M}$ of H_2O_2 was detected and a recovery of $93.0 \pm 2.1\%$ was achieved, suggesting the veracity and feasibility of polyaniline/Cu electrode for environmental analysis.

Conclusion

A nonenzymatic H_2O_2 electrochemical sensor was fabricated by the electrochemical deposition of polyaniline film and Cu nanoparticles on the surface of a glassy carbon electrode. The prepared polyaniline/Cu electrode sensor demonstrated a low detection limit, good reproducibility, and stability for H_2O_2 across a broad linear range. The simple and flexible fabrication method for preparing polyaniline/Cu-based H_2O_2 sensor showed great potential for practical applications.

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