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A novel hydrogen peroxide sensor based on Ag nanoparticles electrodeposited on DNA-networks modified glassy carbon electrode

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Abstract

A novel strategy to fabricate hydrogen peroxide (H_2O_2) sensor was developed by electrodepositing Ag nanoparticles (NPs) on a glassy carbon electrode modified with three-dimensional DNA networks. The result of electrochemical experiments showed that such constructed sensor had a favorable catalytic ability to reduction of H_2O_2. The well catalytic activity of the sensor was ascribed to the DNA networks that facilitated the formation and homogenous distribution of small Ag NPs. The resulted sensor achieved 95% of the steady-state current within 2 s and had a 1.7 μM detection limit of H_2O_2.

Keywords: Sensor; Electrodeposition; Ag nanoparticles; DNA networks; H_2O_2

1. Introduction

Over the last decade, there has been a considerable interest in the accurate determination of hydrogen peroxide (H_2O_2) because it is an essential mediator in food, pharmaceutical, clinical and environmental analysis. Many techniques including titrimetry [1], spectrometry [2] and chemiluminescence [3] have been employed in the determination of H_2O_2. However, these techniques are obviously time-consuming and expensive. Recently, more attention has been paid to the electrochemistry technique owing to its intrinsic sensitivity, high selectivity and simplicity [4,5].

Electrochemistry technique based on a simple and low-cost enzyme electrode has been extensively employed for accurate determination of H_2O_2 because of the intrinsic selectivity and sensitivity of enzymatic reactions [6–8]. Although, a lot of materials have been used to immobilize enzyme on an electrode for retaining the enzymatic biologic activity and electrically connecting the enzyme with the electrode surface, it was ineluctable that these materials might block the electron transfer and biologic activity of the enzyme [9,10].

Inorganic materials modified electrode in determination of H_2O_2 is attracting more and more attention owing to its stability and convenience of electron transfer. Some inorganic materials (such as hexacyanoferrate [11], prussian blue-modified Au nanoparticles (NPs) [12], Pt NPs [13–15], nickel hexacyanoferrate [16] and perovskite-type oxide [17]), inorganic-organic composite materials [18–20], and inorganic-incorporated biology complex membranes [21–25] have been used for the preparation of H_2O_2 sensor. Recent studies have showed that Ag NPs exhibited catalytic activity for H_2O_2 [26]. The size and the distribution of Ag NPs played a vital role in the catalytic ability for H_2O_2. To obtain a good catalytic ability, electrodeposition of Ag^+ in a solution containing DNA molecules to produce Ag NPs have been developed. However, the size of Ag NPs was about 50 nm and the packed density of Ag NPs was very high, which were unfavorable for catalytic ability due to the decrease of catalytic sites.

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In this manuscript, we have exploited Ag NPs electrodeposited on three-dimensional DNA networks that were directly dropped on the surface of GC electrode as an electrocatalyst to fabricate a H_2O_2 sensor. Thus formed Ag NPs showed very good catalytic ability for the reduction of H_2O_2.

2. Experimental sections

2.1. Materials

λ-DNA was obtained from Sino-American Biotechnology company (Beijing, China). Other chemicals were purchased from Beijing Chemical Reagent (Beijing, China).

2.2. Preparation of the H_2O_2 sensor

After the GC electrode was polished carefully, 10 μL DNA of different concentration was directly dropped onto the pretreated GC electrode and dried at 4 °C for 4 h. And then the electrode was immersed in 0.1 M KNO_3 solution containing 3.0 mM $AgNO_3$ and electrodeposited for different time to obtain Ag NPs modified electrode.

2.3. Electrochemical measurements and apparatus

All electrochemical experiments were performed by a CHI 660C (USA) electrochemical workstation using a conventional three-electrode system with a platinum wire as the auxiliary electrode, and a SCE as the reference electrode. Electrolyte solutions were purged with high purity nitrogen prior to experiments and blanketed with nitrogen during electrochemical experiments.

Atomic force microscopy (AFM) measurements were carried out with an AJ-III (Shanghai Aijian Nanotechnology) in tapping mode. Standard silicon cantilevers (spring constant, 0.6–6 N/m) were used under its resonance frequency (typically, 60–150 kHz).

3. Results and discussion

3.1. Electrodeposition of Ag NPs on DNA network

Cyclic voltammetric (CV) was utilized to monitor the redox behaviors of Ag^+ at bare and DNA networks modified GC electrode. As shown in Fig. 1a, in the solution of 3.0 mM $AgNO_3$ and 0.1 M KNO_3, a bare GC electrode showed a cathodic peak at 0.30 V and a sharp anodic peak at 0.49 V. The cathodic peak was ascribed to the reduction of Ag^+ to form Ag NPs and the anodic peak was attributed to the stripping of the electrodeposited Ag NPs. However, when the DNA networks modified electrode was scanned in the same solution, the redox peak currents extremely depressed and the peak potentials shifted in negative direction (Fig. 1b). The decrease of the redox peak current might result from the blocking effect of the DNA networks on the electron transfer. According to the above redox behaviors, the GC electrode was electrodeposited in this solution for 120 s at −0.1 V to obtain Ag NPs modified electrode.

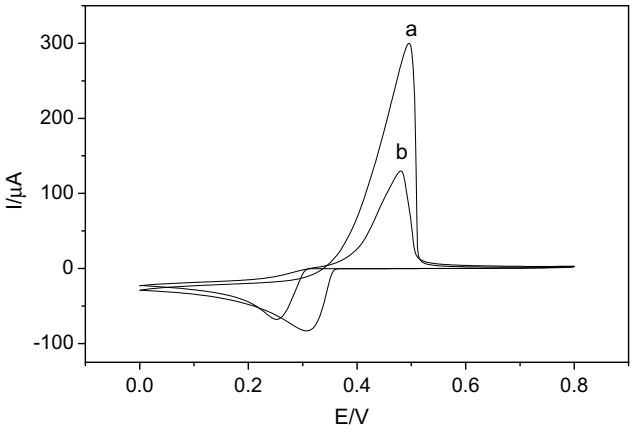

Fig. 1. CV of GC (a) and DNA/GC electrode (b) in the solution of 3.0 mM $AgNO_3$ + 0.1 M KNO_3 at 50 mV/s.

3.2. AFM characterization of the sensor construction

Fig. 2a was the AFM image of the bare GC substrate, showing a smooth and homogeneous surface. Then DNA molecules were immobilized on the GC substrate and formed a network (Fig. 2b) which provided a three-dimensional medium to facilitate the homogenous distribution of Ag NPs (Fig. 2d). Section analysis revealed that the average size of these Ag NPs was about 10 nm (Fig. 2f). In contrast, in the absence of DNA networks, Ag NPs had rather large mean size (about 30 nm, Fig. 2e) with low density, and their distribution was also inhomogeneous (Fig. 2c).

3.3. Amperometric response to H_2O_2

In the presence of 1.0 mM H_2O_2, an obviously catalytic current appeared for the Ag NPs/ DNA/GC electrode (Fig. 3e). The peak potentials appeared at −0.48 V and shifted positively as compared with that of the Ag NPs/ GC electrode (Fig. 3d). The responses of H_2O_2 for the bare GC and DNA/GC electrode were obviously weak and even disregarded (Fig. 3b and c). These results showed that the Ag NPs/DNA/GC electrode possessed the relatively remarkable catalytic ability to H_2O_2 reduction, and the catalytic current mainly resulted from the Ag NPs on the electrocatalytic reduction of H_2O_2.

3.4. Optimization of experimental variables

The effect of DNA concentration on the electrocatalytic reduction of H_2O_2 was investigated in Fig. 4a. There was a remarkable increase in the current response with the increasing DNA concentration and reached the maximal value with 100 ng/L DNA. After that, the steady-state current decreased gradually with further increased DNA concentration.