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Electrocatalytic activity of polymer-stabilized silver nanoclusters for hydrogen peroxide reduction

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ABSTRACT

Silver nanoclusters (AgNCs) synthesized by using polyethyleneimine as a stabilizing scaffold have been confirmed as a novel material to exhibit high electrocatalytic activity for the reduction of hydrogen peroxide in this paper. The novel hydrogen peroxide electrochemical sensor was originally prepared based on the excellent electrocatalytic activity for the reduction of hydrogen peroxide at the polyethyleneimine-templated silver nanoclusters modified glassy carbon electrode (PEI/AgNCs–GCE). To achieve the optimum electrocatalytic activity for the reduction of hydrogen peroxide, the pH of the buffer solution and concentration of immobilizing AgNCs solution were optimized. Under optimum conditions, the PEI/AgNCs–GCE revealed a highly linear response to H_2O_2 in the concentration of 10–1440 μmol L^{-1} with a detection limit of 1.8 μmol L^{-1}. Compared to some silver nanoparticles modified electrodes, the novel electrochemical sensor based on AgNCs exhibited a better electrocatalytic activity for the reduction of H_2O_2 and a lower detection limit for the determination of H_2O_2.

1. Introduction

Hydrogen peroxide is a chemical threat to the environment, which is making the determination of hydrogen peroxide important in various fields including environmental, clinic, food, and pharmaceutical analysis [1]. It is also the production of enzymatic reaction, which can be used in the field of biosensor. Recently, the novel kinds of biosensors, such as acetylcholine biosensor [2] and glucose biosensor [3], are prepared more and more based on the development of H_2O_2 sensors. Among all of analytical methods of accurate and reliable determination of H_2O_2 including titrimetry [4], fluorometry [5], and electrochemistry [6], electroanalytical techniques have emerged as preferable methods because of their advantages of efficiency, high sensitivity, simple operation, and low cost.

Few-atom noble metal nanoclusters, typically consisting of several to tens of atoms, are novel fluorescent nanomaterials that have aroused a great deal of consideration. But without stabilizer, metal nanoclusters would strongly interact with each other and aggregate irreversibly to form nanoparticles for reducing their surface energy [7]. Recently, silver nanoclusters (AgNCs) stabilized by various templates [8–11], such as biomolecules, thiolates, polyelectrolytes, and DNA, have received significant attention for biological applications due to their useful properties, including high molar absorptivity, good quantum yield, outstanding photostability, and small size [12–15]. The researches of silver nanoclusters as a kind of fluorescence probe are also considered as the most concerned topics. At present, silver nanoclusters are widely used in the aspects of light scattering [16], fluorescence [17], chemiluminescence [18], and electroluminescence [19] for their excellent optical properties. And even so much excellent properties owned by the silver nanoclusters have been found, there are also some other great properties of silver nanoclusters being considered with little attention, such as the electrocatalytic activity, and silver nanoclusters are rarely used in the field of electrochemistry. It is known that silver nanoparticles showed excellent electrocatalytic activity and were widely used to the preparation of silver nanoparticles modified electrochemical sensors for the detection of H_2O_2 and some nitroaromatic compounds [20]. However, compared to silver nanoparticles, AgNCs can offer higher electrocatalytic activity due to their larger specific surface area.

To our best knowledge, there is no paper reporting the reasearch about the electrocatalytic activity of AgNCs stabilized by polyethyleneimine (PEI). In this paper, to conduct the research about the electrocatalytic activity of AgNCs, silver nanoclusters were synthesized using PEI as a stabilizing scaffold and originally used to the preparation of modified glassy carbon electrode (PEI/AgNCs–GCE) for the electrochemical determination of H_2O_2 (Scheme 1). The PEI-stabilized AgNCs modified glassy carbon electrode was fabricated for the first time and used to the determination of H_2O_2 based on the excellent electrocatalytic activity of AgNCs for the reduction of H_2O_2.

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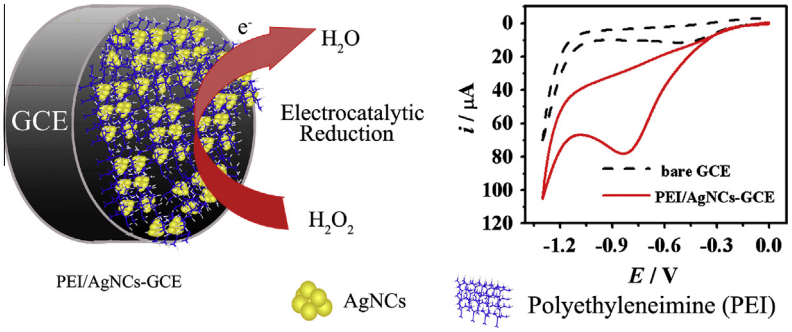

Scheme 1. Electrocatalytic reduction of H_2O_2 at the polyethyleneimine-templated silver nanoclusters modified glassy carbon electrode.

2. Experimental

2.1. Reagents and chemicals

Silver nitrate ($AgNO_3$), hyperbranched polyethyleneimine (PEI, M_W = 10,000, 99%), 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), formaldehyde (35 wt%), dopamine, and l-ascorbic acid were purchased from Aladdin Reagent Co., Ltd., Shanghai, China. Uric acid and glucose were obtained from Sigma-Aldrich Co., USA. Hydrogen peroxide (30%), potassium chloride, sodium biphosphate dehydrate, and disodium hydrogen phosphate dodecahydrate were purchased from Chengdu Kelong Chemical Reagents Co., Ltd. (Chengdu, China) and used as received. Phosphate buffer solutions giving the pH required were prepared by step-wise adjustment of 0.10 mol L^{-1} NaH_2PO_4 and 0.10 mol L^{-1} Na_2HPO_4 solutions. All solutions were freshly prepared before use, and Milli-Q water (18 MΩ cm) was used throughout the experiments.

2.2. Apparatus

A CHI 660B electrochemical station (CHEN HUA Instruments Co., Shanghai, China) was employed for the electrochemical measurements including cyclic voltammetry (CV), chronoamperometry, and electrochemical impedance spectroscopy (EIS). A three-electrode system consisted of a modified glassy carbon working electrode with diameter of 3 mm, a saturated Ag/AgCl reference electrode, and an auxiliary electrode made of platinum. All electrochemical measurements were carried out in a 10 mL cell. All potentials were given with respect to the Ag/AgCl electrode. A rapid mixing device (Ronghua Instrument Plant, Jiangsu, China) was used to mix solution completely for the dilution of original AgNCs solution. A pHs-3B pH meter (Dazhong, Shanghai, China) was used for measuring pH.

2.3. Synthesis procedure

Using PEI as a template, the AgNCs were synthesized according to our previous works [21,22]. Firstly, 100 μL of 0.094 g mL^{-1} PEI and 50 μL of 1 mmol L^{-1} HEPES solution were dissolved in water by stirring for 2 min, and then 250 μL of 100 mmol L^{-1} $AgNO_3$ was added and homogenized by stirring for 2 min. Next, 5 μL of formaldehyde solution was added under vigorous stirring and the mixture was heated at 70 °C for 10 min. Finally, Ag nanoclusters solution was stocked at ambient environment for at least 48 h before its further application. Without any centrifugation or purification, the PEI-stabilized Ag nanoclusters solutions were diluted 50-fold in water, and the diluted Ag nanoclusters solutions were applied to the preparation of modified electrode.

2.4. Preparation of silver nanoclusters modified glassy carbon electrode

Prior to the preparation of modified electrode, the glassy carbon electrode was mechanically polished with 0.3 and 0.05 μm alumina slurry to a mirror finish, respectively, rinsed and sonicated in doubly distilled water for 5 min. And then the glassy carbon electrode was scanned by cyclic voltammetry from −0.9 to +0.9 V in phosphate buffer solution until repeating cyclic voltammograms appeared. AgNCs were immobilized onto a polished glassy carbon electrode using the solution of PEI-stabilized AgNCs for the preparation of PEI/AgNCs–GCE. An aliquot of 5 μL silver nanoclusters solution containing 1 mmol L^{-1} AgNCs and 1.88 mg mL^{-1} PEI gotten through the 50-fold dilution of original solution was dropped on the surface of glassy carbon electrode and dried with nitrogen gas at room temperature (25 °C) for 1 h. For the experiment of comparison, the PEI modified electrode (PEI–GCE) was also prepared under the same conditions in the absence of AgNCs.

2.5. Electroanalytical measurements

Electrochemical characterization of the modified electrodes was carried out in 5.0 mmol L^{-1} $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ solution containing 0.1 mol L^{-1} KCl using CV and EIS techniques at room temperature (25 °C). Voltage frequencies used for EIS measurements ranged from 10 kHz to 100 mHz, and the ac voltage amplitude was 5 mV. Cyclic voltammetric and chronoamperometric measurements were carried out in 0.1 mol L^{-1} phosphate buffer solution with a three-electrode cell. Before the measurements, the supporting electrolytes were purged with nitrogen for 5 min. Current measurements were performed using CV in the potential range between 0 and −1.3 V and scan rate of 50 mV s^{-1}. To record the chronoamperometric measurements, the following instrumental parameters were used: Pulse width of 1000 s, sample interval of 0.1 s, and potential of −0.78 V.

3. Results and discussion

3.1. Characterization of silver nanoclusters modified glassy carbon electrode

The 0.05 mol L^{-1} water-soluble and stable silver nanoclusters were synthesized on the basis of a PEI-modified silver mirror reaction. The silver nanoclusters were characterized using UV–vis spectroscopy, fluorescence spectroscopy, X-ray diffraction technique, and high resolution transmission electron microscopy (HRTEM) in our pervious works [5,21,22]. And the results showed that the PEI-capped silver nanoclusters had an absorption band centered at 354 nm in the UV–vis absorption spectrum. The fluorescene