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Porphyrin-functionalized gold nanoparticles for selective electrochemical detection of peroxyacetic acid

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ABSTRACT

Two layers of cationic iron(III) meso-tetrakis (N-methylpyridinum-4-yl)porphyrin (FeTMPyP) and anionic gold nanoparticles (GNPs) were alternately assembled on a poly(diallyldimethylammonium chloride)-wrapped carbon nanotube (PDDA-CNT)-modified electrode via electrostatic interactions. The porphyrin-functionalized gold nanoparticles were characterized by scanning electron microscopy and UV–vis absorption spectrometry. The $(FeTMPyP–GNP)_2$/PDDA-CNT modified electrode showed two stable and well-defined peaks at −0.112 V and −0.154 V, which were attributed to the GNP-accelerated redox process of Fe(III)TMPyP/Fe(II)TMPyP. The modified electrode possessed excellent electrocatalytic behavior for the reduction of peroxyacetic acid (PAA). The resulting biosensor exhibited a fast amperometric response to PAA (~3 s), with a wide linear range from 2.5×10^{-6} M to 1.05×10^{-3} M and a detection limit of 0.5 μM at a signal-to-noise ratio of 3. More importantly, H_2O_2 did not interfere with the detection. Thus, this biosensor enabled highly sensitive detection of PAA without removing H_2O_2 and showed a promising potential in practical applications.

1. Introduction

Peroxyacetic acid (PAA) is widely used in the food and cleaning industries as an ideal disinfectant [1], as its strong oxidizing power can rapidly kill all microorganisms such as viruses, bacteria, fungi, and spores. However, a high concentration of PAA may cause skin and mucosal irritation in humans and even cause burns. Thus, there exists a need for a quick and easy method for the detection of PAA. Several methods have been developed for PAA detection, such as titration [2], photometry [3], spectroscopy [4], and gas or liquid chromatography [5–8]. Although these methods have adequate sensitivity, they often suffer from the need for time-consuming derivatization and extraction steps. To make use of the advantages of electrochemical analysis, Ohsaka and coworkers [9] developed a novel electroanalytical method for PAA detection in the presence of H_2O_2 using a rotating gold-disk electrode. Bontempelli and coworkers [10] then used a rotating Pt- or gold-disk electrode to further study the electrochemical behaviors of PAA and H_2O_2 and achieved the selective detection of PAA and H_2O_2 in cosolution. However, rotating disk electrodes are obviously difficult to use for *in situ* or online monitoring. Thus, it is of interest to seek an efficient catalyst for the selective detection of PAA.

Porphyrins are an important class of conjugated organic molecules and have been employed to mimic the active sites of many important enzymes, such as hemoglobin, myoglobin, cytochrome *c* oxidase [11], nitric oxide reductase [12], vitamin B_{12} [13], and chlorophyll [14]. The metalloporphyrins, especially iron porphyrins, can be used as electronic media based on their reversible Fe(III)/Fe(II) redox states and exhibit good electrocatalysis for biologically important molecules [15–19], including dissolved oxygen [15,16], NO [17–19], and nitrite [12]. Thus, we studied the electrocatalytic activity of iron(III) meso-tetrakis (N-methylpyridinum-4-yl)porphyrin (FeTMPyP) for the reduction of PAA and H_2O_2 by assembling alternate layers of FeTMPyP and gold nanoparticles (GNPs) on a poly(diallyldimethylammonium chloride)-wrapped carbon nanotube (PDDA-CNT)-modified electrode.

Porphyrin-functionalized nanoparticles are expected to have significantly different chemical activities from those of free porphyrins [20–23]. The controlled organization of functional porphyrins into highly ordered nanomaterials has showed great potential in photoelectrochemical applications by improving the photoelectrochemical transfer efficiency [24–29]. Furthermore, their application to electrochemical biosensing has attracted considerable attention. Dong and coworkers [30] reported the elaboration of a nanocomposite of GNPs and porphyrin by depositing anionic $AuCl_4^-$ and cationic cobalt porphyrin onto an ITO substrate followed by electrochemical reduction. In previous work, we designed a series of porphyrin-functionalized carbon nano-

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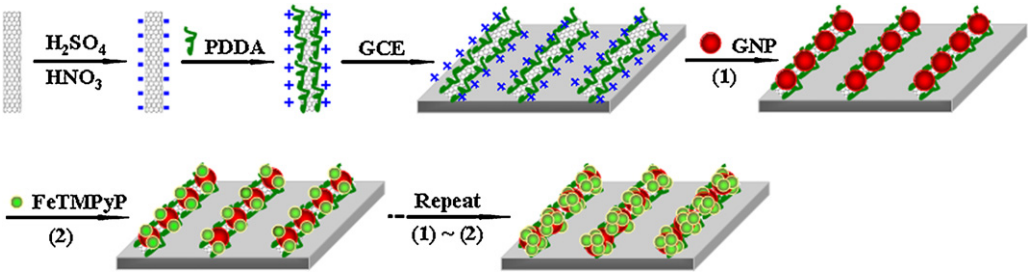

Scheme 1. Assembly process of FeTMPyP–GNPs on the PDDA-CNT-modified GCE.

materials and developed several electrocatalytic methods for the detection of biological molecules, such as trichloroacetic acid [31], chloramphenicol [32], sulfite [33], and chlorite [34].

Here, the FeTMPyP-functionalized GNPs assembled on PDDA-CNTs via electrostatic interactions showed well-defined redox peaks of Fe(III)TMPyP/Fe(II)TMPyP. The GNPs accelerated the electron transfer between FeTMPyP and the electrode, and the PDDA-CNTs insured the immobilization of the functionalized GNPs on the electrode surface. The modified electrode showed a high overpotential for the reduction of hydrogen peroxide and a sensitive response to PAA reduction because of the excellent electrocatalytic activity of FeTMPyP-functionalized GNPs, leading to a highly selective amperometric biosensor for PAA. This biosensor was successfully applied in the amperometric detection of PAA in a disinfectant sample and could provide a novel biosensing tool for environmental monitoring.

2. Experimental

2.1. Materials and reagents

FeTMPyP was a gift from Kanazawa University (Japan). Chloroauric acid ($HAuCl_4{\cdot}4H_2O$) and trisodium citrate were obtained from Shanghai Reagent Company (Shanghai, China). Multiwalled carbon nanotubes (CNTs; CVD method, purity ≥98%, diameter 20–40 nm, and length 1–2 μm) were purchased from Nanoport Co. Ltd. (Shenzhen, China). PAA was purchased from the Tongzhi Trade, Limited, Company (Shanghai, China). Poly(diallyldimethylammonium chloride) (PDDA; 20%, w/w in water, MW: 200,000–350,000) was obtained from Sigma–Aldrich Chemical Co. (St. Louis, MO). Phosphate-buffered saline (PBS, 0.1 M) solutions were prepared at various pH values by mixing stock solutions of NaH_2PO_4 and Na_2HPO_4. Ultrapure water obtained from a Millipore water-purification system (≥18 MΩ, Milli-Q, Millipore) was used in all assays. All other reagents were of analytical grade and used as received.

2.2. Apparatus

Electrochemical measurements were performed on a CHI 812B electrochemical analyzer (Co., CHI, USA) with a conventional three-electrode system. A glassy carbon electrode (GCE) (diameter 3 mm), a saturated calomel electrode (SCE), and a Pt electrode were used as the working electrode, reference electrode, and an auxiliary electrode, respectively. Scanning electron micrographs (SEMs) were obtained with a Hitachi S-3000N scanning electron microscope (Japan) at an acceleration voltage of 10 kV. The UV–vis spectra were measured with a UV-3600 UV–vis spectrophotometer (Shimadzu, Japan).

2.3. Fabrication of the biosensors

Colloidal GNPs 15 nm in diameter were prepared by quickly adding 2.5 mL 1% trisodium citrate to 100 mL of a boiling 0.01% $HAuCl_4$ solution and stirring the solution until deep red [35]. The PDDA-CNT composite was synthesized as described in our previous work [36]. The CNTs were first treated with 3:1 H_2SO_4/HNO_3 under sonication for 4 h to shorten the CNTs, remove metallic and carbonaceous impurities, and generate carboxylate groups on the CNT surfaces. Next, 0.5 mg mL^{-1} of the carboxylated CNTs was dispersed into a 0.20% PDDA aqueous solution containing 0.5 M NaCl by sonication for 30 min to give a homogeneous black suspension. After washing with water, the composite was dispersed into water to yield 0.5 mg mL^{-1} PDDA-CNTs.

The fabrication procedure for the biosensors is shown in Scheme 1. Prior to modification, the GCE was successively polished to a mirror finish using 1.0- and 0.05-μm alumina slurry (Beuhler). After successive sonication in ethanol and double-distilled water, the electrode was rinsed with double-distilled water and allowed to dry at room temperature. After casting 3 μL of PDDA-CNT (0.5 mg mL^{-1}) onto the surface, 4 μL of GNPs was dropped onto the electrode. After removing the unadsorbed GNPs, a negatively charged surface was formed for the assembly of 4 μL of FeTMPyP (400 μM). Afterwards, another layer of FeTMPyP–GNPs was assembled on the first layer of FeTMPyP–GNPs by the same casting of GNPs and FeTMPyP. In this way, the multilayer FeTMPyP–GNP coating was obtained.

3. Results and discussion

3.1. Characterization of FeTMPyP–GNP assembly

Because of their high surface-to-volume ratio and excellent conductivity, CNTs have been extensively investigated as essential carriers in the constructing of electrochemical biosensors by wrapping cationic PDDA on the sidewall surface of the carboxylated CNTs to facilitate loading the negatively charged materials. Fig. 1 shows SEM images of the CNTs, PDDA-CNTs, GNPs/PDDA-CNTs and $(FeTMPyP–GNPs)_2$/PDDA-CNTs on ITO substrates. The carboxylated CNTs obtained by chemical oxidation exhibited a homogeneous and even dispersion, with a diameter of around 30 nm (Fig. 1A). After wrapping with PDDA, the diameter of the CNTs did not show an obvious change (Fig. 1B). After assembly of the negatively charged GNPs, densely packed GNPs were observed on the surface of the PDDA-CNTs, with a slight increase in size (Fig. 1C). After two layers of FeTMPyP–GNPs were assembled, a more densely packed morphology was observed, as in Fig. 1D.

To further identify the interaction between GNPs and FeTMPyP, the UV–vis spectra of FeTMPyP, GNPs and FeTMPyP–GNPs were examined (Fig. 2). The characteristic absorption peaks of FeTMPyP and GNPs were at 422 nm and 519 nm, which corresponded to the Soret band of FeTMPyP and the plasmon band of GNPs, respec-