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In situ electropolymerised silica–polyaniline core–shell structures: Electrode modification and enzyme biosensor enhancement

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Abstract

Micro- and nanostructured electrode interfaces have the potential to exhibit improved performance characteristics. Here, we illustrate the interaction of an electropolymerised polyaniline film with silica microparticles on glassy carbon electrodes. It was found that the polyaniline grew preferentially around the silica particles rather than on the underlying electrode surface. This was found to be due to the adsorption of aniline monomers onto the silica surface, followed by in situ electropolymerisation. The thickness of the PANI layer could be controlled through the adjustment of polymerisation time from several to many tens of nanometres.

In conjunction with immobilisation of the enzyme, horseradish peroxidase (HRP), the electrocatalytic reduction of hydrogen peroxide was found to be enhanced under certain conditions over polymer films grown in the absence of silica particles. It is believed that this may be due to the special structure of the silica–PANI core–shell particles. Silica particles coated with a nanofilm of PANI appear to adsorb HRP more effectively, while also increasing the active electrode surface area.

Keywords: Silica particles; Polyaniline; Electropolymerisation; Biosensor; Horseradish peroxidase

1. Introduction

Polyaniline (PANI), as a key material in the family of conducting polymers, has attracted intensive interest due to its promising electrical, electrochemical and optical properties [1]. Numerous applications of this conducting polymer have been reported in the past years, and among the most promising applications of PANI are electrochemical sensing and biosensing [2–5]. PANI can provide a suitable environment for the immobilization of biomolecules, and the resulting PANI-modified electrodes have several advantages such as impressive signal amplification and elimination of electrode fouling. Due to its excellent conductivity and electroactivity, PANI can act as a mediator for enzyme electrodes, where PANI undergoes redox cycling and can couple electrons directly from the enzyme active site to the electrode surface [6,7].

To prepare PANI-modified electrodes, the most convenient and popular way is the electropolymerisation of aniline, through galvanostatic, potentiostatic or potentiodynamic means, as it offers the potential to incorporate a wide range of dopants into the formed PANI film and gives good control over film thickness [8]. In recent years, different materials, most notably nanomaterials, have been incorporated or embedded into PANI films during electropolymerisation in order to enhance the properties of the resulting composite materials. For example, carbon nanotube/PANI hybrid systems can be constructed either by the electropolymerisation of the aniline monomer with functionalised carbon nanotubes as dopants [9], or through the electropolymerisation of the aniline monomer on carbon nanotube-modified electrodes [10]. Gold nanoparticle/PANI hybrid systems have also been prepared through the electropolymerisation of the aniline monomer in the presence of negatively charged sulfonate-functionalized gold nanoparticles [11]. Hybrid systems consisting of PANI and other materials, such as platinum nanoparticles [12] and carbon particles [13] have also been prepared through electropolymerisation.

Silica particles have been extensively used as stabilizers in the preparation of PANI dispersions or colloids [14–16], and different hybrid systems consisting of PANI and silica particles have been reported [17–19]. To date, the silica particle/PANI hybrid

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systems have mostly been constructed through the chemical polymerization of aniline in the presence of the silica particles, or sometimes by modifying the silica particles with PANI prepared in advance [20]. Compared with electropolymerisation, these methods are inconvenient in controlling the thickness of the formed PANI films and constructing modified electrodes. However, due to the chemical inertness and non-conductivity of silica particles, it might be considered difficult to carry out electropolymerisation of aniline around the surface of silica particles. However, in this work, a silica particle/PANI hybrid system consisting of silica particles covered with PANI nanofilm was constructed on a glassy carbon electrode surface through a facile electrochemical method. A possible formation mechanism and biosensor application, as well as SEM characterization of this hybrid system were also investigated.

2. Experimental

2.1. Chemicals and materials

HRP (200 U mg^{-1}, P6782) and tetraethylortho-silicate (TEOS) were purchased from Sigma–Aldrich. Aniline was purchased from Aldrich (13,293-4), vacuum distilled and stored frozen under nitrogen. Thirty percent (v/v) hydrogen peroxide solution (108,597) was from Merck (Darmstadt, Germany), and standard hydrogen peroxide solutions were prepared daily. Poly(vinylsulfonic acid) sodium salt (PVS, 27,842-4) was purchased from Aldrich. All other chemicals were of analytical grade, and Milli-Q water (resistance over 18 MΩ cm) from a Millipore Q water purification system was used throughout.

Silica particles with the diameter of about 250 nm were prepared by controlled hydrolysis of TEOS in the mixture of ethanol and ammonium hydroxide according to Luo et al. [21]. Considering the amount of starting material, the density of silica, and the approximate size of the silica particles, and assuming that the reaction yield was 100%, the number of silica particles per millilitre was calculated to be 7.66×10^{11}. That is, the concentration of the as-prepared silica particle suspension was about 1.27 nM. If necessary, the silica particle suspension was diluted to different concentrations, 0.64, 0.32 and 0.16 nM with water.

2.2. Instrumentation

Electrochemical experiments were performed on a CHI 1000 electrochemical workstation (CH Instruments, USA) using a conventional three-electrode system with the modified electrode as the working electrode, a platinum mesh as the auxiliary electrode, and a silver/silver chloride (Ag/AgCl) reference electrode (purchased from Bioanalytical Systems Ltd., UK).

Scanning electron microscopy (SEM) was performed with a Hitachi S3000N scanning electron microscope. An acceleration voltage of 20 kV was employed.

2.3. Preparation of the modified electrodes

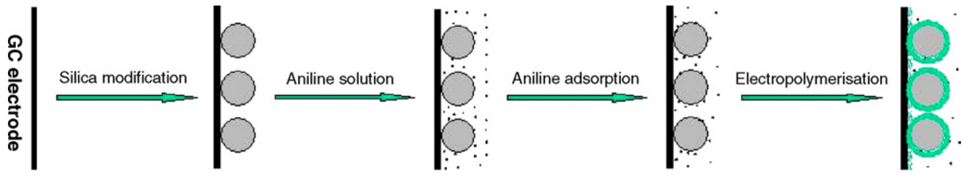
Glassy carbon electrodes (3 mm in diameter) were polished with 1.0, 0.3 and 0.05 μm alumina slurry in sequence and then ultrasonically washed in water and ethanol for about 5 min, respectively. About 2.0 μL silica particle suspension (0.32 nM, if not stated) was dropped onto the cleaned glassy carbon electrode surface with a pipette. After the evaporation of the water in air, silica particles became deposited on most of the electrode surface, except for a thicker ring of silica particles which formed around the very edge of the glassy carbon electrode as a result of the drying process. The resulting silica particle-modified electrodes were used for electropolymerisation of aniline.

A mixture of 4.0 mL 1.0 M HCl, 9.1 μL distilled pure aniline and 1.0 mL PVS was degassed under nitrogen for about 10 min. Before electropolymerisation, the silica particle-modified electrode was dipped into the mixture and kept for 2 min. The electropolymerisation of aniline was then carried out at a constant potential of +0.9 V for a certain period of time, and PANI was thus formed on the electrode surface and around the surface of silica particles. The procedure of preparing the modified electrode is shown in Scheme 1. After electropolymerisation of aniline, the electrode was washed with 1.0 M HCl and water and dried in air.

For the construction of the biosensor, 5 μL HRP solution (2.0 mg mL^{-1}, in pH 7.4 PBS) was dropped onto the surface of the modified electrode, and when it was dried in air, the electrode was rinsed with water to remove excess enzyme. The resulting electrode was denoted as HRP/PANI/SiO_2/GC electrode. For comparison, modified electrodes without silica particles were prepared and denoted as HRP/PANI/GC electrode. All the prepared electrodes were stored at 4 °C in a refrigerator when not in use.

2.4. Electrochemical measurements

The electrochemical behaviour of the PANI-modified electrode was investigated by cyclic voltammetry in the potential range between −0.2 and +0.8 V in 1.0 M HCl solution. Amperometric determination of H_2O_2 was carried out at an applied potential of −100 mV under magnetic stirring in pH 7.4 phosphate buffer solution (PBS, 0.1 M phosphate, 0.137 M NaCl and 2.7 mM KCl). After the background current reached a considerably steady value, standard hydrogen peroxide solutions were injected into the detection solution, and the steady state currents



Scheme 1. Procedure of the preparation of the PANI covered silica particles.