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Nanoelectrode ensembles based on conductive polyaniline/poly(acrylic acid) using porous sol–gel films as template

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Abstract

Porous sol–gel (PSG) film has been utilized as a template for the electrochemical polymerization of aniline in presence of poly(acrylic acid) (PAA). The presence of electroactive polyaniline (PAn)/PAA within the porous skeleton of the sol–gel films has been confirmed using cyclic voltammetry, UV–vis spectrometry and atomic force microscopic measurements. The densities and the sizes of the nanoelectrodes can be controlled easily using electrochemical methods. The conductive polymer "wires" of PAn/PAA formation in PSG matrix can behave as an ensemble of closely-spaced but isolated nanoelectrodes. Moreover, the nanoelectrode ensembles based on conductive PAn/PAA for glucose biosensing are fabricated by immobilization of glucose oxidase (GOx) and Nafion onto the surface of conductive polymer. Owing to the biocompatibility of PSG and electro-activity of PAn/PAA at neutral pH regions, the glucose biosensor shows excellent characteristics and performance, such as low detection limit and fast response time.

Keywords: Nanoelectrode ensembles; Polyaniline/poly(acrylic acid); Porous sol–gel film; Template synthesis; Glucose biosensor

1. Introduction

Recently, efforts towards structuring ordered materials have been made during the process of research on conducting polymers because of many improved properties (high conductivity, high mobility) will be expected from these ordered structures [1–5]. Among the conducting polymers, polyaniline (PAn) is an excellent candidate for organic molecular due to its controllable electrical conductivity, ease of preparation, good environmental stability and interesting redox properties [6]. Nanostructured PAn has been synthesized both chemically and electrochemically through polymerization of the monomer by the template method [7–9], the template-free method [10,11] and physical methods such as electrospinning [12] and mechanical stretching [13]. Among above mentioned methods, template methods have been shown to offer an effective approach for the fabrication of structured materials with unique properties that are difficult to produce by traditional patterning procedures [14–16]. The templates normally used include diblock copolymers [17], anodized alumina layers [18], organic or inorganic colloidal crystals [19,20], and others [21].

The sol–gel process is a very powerful tool for preparing excellent organic/inorganic hybrids, and this process has been used to prepare conducting PAn/silica hybrids [22]. However, all these hybrids were prepared in high boiling point or toxic solvents. Considering the increasing environmental concern about volatile compounds evolved during processing, conductive PAn/silicate hybrids via in-situ hydrolysis and polycondensation of tetraethoxysilane (TEOS) in aqueous conductive PAn solution were prepared [23]. sol–gels can also be engineered to form porous thin film and structured electronically conductive materials are available by chemical or electrochemical polymerization using sol–gel films as template. In addition, the conducting polymer growth in sol–gel films could be used as micro- or nanoelectrode arrays. Verghese et al. [24] demonstrated

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that the PAn growth in the TEOS sol–gel matrix could behave as "molecular wires" and have potential application as a nanoelectrode. Poly(3,4-ethylenedioxythiophene) (PEDOT), which grown in porous TEOS/methyltriethoxysilane sol–gel films, was also prepared by electropolymerization, and the emergent conducting polymer wires could act as ultramicroelectrode arrays [25].

In the present paper, we aim to design nanoelectrode ensembles (NEEs) for glucose biosensing, which are based on growth PAn into porous sol–gel (PSG) films using electrochemical technique. However, PAn exhibits redox-active only in acidic solutions, which limits its broad use, specifically in biosensing. Fortunately, the redox activity of PAn can be sustained in neutral pH solutions by doping it with different polyanions, such as poly(acrylic acid) (PAA), poly(styrene sulfonate) (PSS), or poly(vinyl sulfonate) (PVS) [26–29]. As well known, the emeraldine form of PAn is usually deprotonated and non-conducting at neutral pH, however, if the polymeric counter anions are entrapped within the PAn films, the pH value for deprotonation is higher than that of the HCl salts of substituted PAn. In other words, the incorporation of the polyanions into the PAn film shifted the p*K*a of the emeraldine form of PAn to a higher pH so that the film remained sufficiently conducting at pH 7.0 [30]. In our work, the surface modification of PAn was performed through graft copolymerization with PAA using PSG films as template and ordered PAn/PAA nanostructure was obtained. The ordered PAn/PAA behaves as ensembles of closely-spaced but isolated nanoelectrodes for glucose sensing. Moreover, the structured PAn/PAA, which was grown from PSG film, shows more sensitive response for glucose than random distributed PAn/PAA prepared without template.

2. Experimental

2.1. Reagents

TEOS (99%, Shanghai Reagent Company), Aniline (An, Shanghai No 3 Reagent Co, three-distilled), PAA (450000 g/mol, Aldrich), Hexadecyltrimethylammonium bromide (CTAB, Beijing Midwest Chemical Factory), Glucose oxidase (GOx, EC 1.1.3.4, 133600 units/g, type VII-S from *Aspergillus niger*, Sigma), β-D-Glucose (Runjie, Shanghai), Bovine serum albumin (BSA, lizhudongfeng biological technical company, Shanghai) were used without further purification.

Twenty-five percent Glutaraldehyde (GA) water solution, 30% H_2O_2 (Shanghai Chemical reagent company) and 1% Nafion solution (Aldrich) were also be used. Potassium phosphate buffer solution (PBS, 0.1 M, pH 6.9) was used as buffer solution.

2.2. Apparatus

Atomic force microscopic (AFM) measurements were performed in tapping mode on a Digital Instruments Multimode III instrument (nanoscope III, USA). UV–vis spectrum was obtained by a Cary 50 UV–vis spectrophotometer (varian, Australia).

All electrochemical experiments were carried out with a CHI-832 electrochemical workstation (CH Instruments, USA). A conventional three-electrode cell, with a bare glassy carbon (GC) electrode (2 mm diameter, BAS Co., Japan), indium–tin oxide (ITO) or modified GC electrode as the working electrode, a saturated calomel electrode (SCE) (Jiangsu Electroanalytical Instruments Factory, China) as the reference electrode, and a platinum electrode as the auxiliary electrode, was used for electrochemical experiments. All potentials in this paper referred to the potential of the SCE reference electrode.

2.3. Preparation of TEOS-derived porous sol–gel silica film

The preparation of sol–gel solution accorded with a reported procedure [31]. In briefly, sol–gel thin films were made from a precursor sol formulation consisting of 600 μL of methanol, 50 μL of TEOS, 10 μL of 3.8% CTAB solution and 60 μL of deionized water, and 10 μL of 5.0 mM NaOH as catalyst. Solutions were vigorously stirred at room temperature for 5 min to yield the precursor sol and then cooled to 4 °C immediately. In addition, the sol was used within 4 h of preparation to ensure desired properties. Films were cast immediately by pipetting 3.0 μL of the sol–gel solution onto a cleanly polished GC electrode surface and spin casting at 2500 rpm for 1 min in 10% humidity. Films were allowed to cure at room temperature and humidity (~20%) for approximately 4 h prior to electrochemical characterization.

2.4. Preparation of ordered conducting polymer PAn/PAA

Ordered PAn/PAA composite was prepared by electropolymerization aniline in presence of PAA with PSG as a template. PSG-coated GC electrode was cycled in a solution of 0.2 M of distilled aniline, 15 mg/mL PAA, 0.1 M H_2SO_4 and 0.5 M Na_2SO_4 over the potential range from −0.1 to +1.1 V at 100 mV/s. Then the resulting modified electrode was washed with the background electrolyte solution of 0.1 M H_2SO_4 and 0.5 M Na_2SO_4 to exclude any residual monomer.

2.5. Construction of the glucose biosensor

An enzyme solution containing 229.2 U/mL GOx and 5% BSA was prepared by dissolving approximately 0.5 mg of GOx and 2.5 mg of BSA in 50 μL of PBS. An aliquot of 25 μL of the enzyme solution and 5 μL of 5% GA solution were then mixed thoroughly. Then, 3 μL of the mixture solution was placed onto the modified electrodes. After cross-linked at room temperature for 2 h, the enzyme electrodes were further coated with 3 μL of 1% Nafion for eliminating the interferences of coexisting electroactive compounds. The glucose biosensors were kept in PBS at 4 °C when not use.