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Fabrication and Voltammetric Characters of Carbon Paste Electrode Modified Using Poly-Silk Peptide

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Abstract

A new material poly-silk peptide was fabricated using the electropolymerization of Silk Peptide (SP) on the surface of a Carbon Paste Electrode (CPE) for the first time. The morphological feature of poly-silk peptide film was characterized by Scanning Electron Microscopy (SEM). The preparation conditions such as SP concentration, supporting electrolyte pH and scan cycles were optimized. A stable poly-silk peptide film could be obtained with scanning 16 cycles in pH7.4 Phosphate Buffer Solution (PBS) containing 0.6 $g{\cdot}L^{-1}$ SP between -0.5 and $+1.5$V. In addition, a well-defined pair of oxidative and reductive peaks of poly-silk peptide was observed in 0.1M H_2SO_4 solution (pH 1.1), resulting from the successive redox reaction of —OH, —C═O and —COOH groups on poly-silk peptide.

Keywords: Silk Peptide; Electropolymerization; Carbon Paste Electrode

1 Introduction

Silk fibroin is a natural protein material prepared by silkworm silk. The renewed interest in silk fibroin for biomedical applications [1] including surgery sutures [2], bone-compatible materials [3, 4] and drug carrier [5, 6] is because of its excellent biocompatibility, good permeability to oxygen and water vapor [7, 8] as well as fine mechanical properties [9]. However, as silk fibroin is an indissoluble gel protein, it is easy to immobilize silk fibroin onto the surface of electrode through self-assembly [10], not electrochemical methods. On the other hand, compared with silk fibroin, the product of silk fibroin hydrolysis Silk Peptide (SP) not only dissolves in water, but also keeps the beneficial properties of silk fibroin. Using electrochemical polymerization, it is expected to be able to obtain new material poly-silk peptide (poly-SP) with various special functions. Therefore, in this paper, a new biocompatible film poly-SP was prepared with the electropolymerization of natural SP on the surface of carbon paste electrode. This poly-SP had stable voltammetric response in 0.1M H_2SO_4 solution (pH 1.1), originating from redox reaction of —OH, —C═O and —COOH groups on poly-SP. It will be electrochemical capacitor in the future.

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2 Experimental

2.1 Apparatus and Reagents

All the voltammetric experiments were carried out by a CHI 660 electrochemical work station (CH Instrument Inc., USA) with a three-electrode configuration: a Saturated Calomel reference Electrode (SCE), a Pt wire auxiliary electrode and a carbon paste or modified carbon paste working electrode. SP (the purity >99.99%) was purchased from Zhejiang Silk Science Institute, China. Stock SP solution (2 g $\cdot$ L^{-1}) was prepared by dissolving SP with twice distilled water and stocked in 4 °C refrigerator. Scanning Electron Microscopic (SEM) measurements were performed on a Field Emission Scanning Electron Microscope JSM-6700F (JEOL, Japan) at 10 kV voltage. All other chemicals were of analytical-reagent grade or better. Twice distilled water was used throughout the experiments.

2.2 Electrode Preparation

A bare Carbon Paste Electrode (CPE) was prepared as follows: graphite powder and di-methyl silicone oil in a ratio of 7:3 (m/m) was thoroughly mixed, and a portion of it was filled into the cavity of the plastic tube (3.0 mm diameter). Electrical contact to its inner side was established with a copper wire. The electrochemical modification of a CPE called poly-SP was performed in 0.04 M Phosphate Buffer (PBS) (pH 7.4) containing 0.6 g $\cdot$ L^{-1} SP with scanning 16 cycles between -0.5 and $+1.5$ V at a scan rate of 0.1 V $\cdot$ s^{-1}. After the fabrication, the resulting electrodes were washed thoroughly with distilled water twice and dried at room temperature.

Self–assembled–SP–CPE (SA–SP–CPE) preparation: a bare CPE was immersed into 0.04 M PBS (pH 7.4) solution containing 0.6 g $\cdot$ L^{-1} SP for 24 h.

3 Results and Discussion

3.1 Fabrication of poly-SP Film

3.1.1 The Optimum of poly-SP Fabrication Conditions

The electro polymerization condition such as SP concentration, type and pH of supporting electrolyte and cyclic times was investigated. The stable poly-SP was observed in PBS. According to the integration of the cyclic voltammetric oxidative peak and Faraday's laws, the surface coverage concentration ($\acute{\Gamma}$) of poly-SP could be estimated from the following formula: Q=nFA$\acute{\Gamma}$, where Q is the total amount of charge passed through the electrode for the oxidative reaction, A is the electrode area, n and F were of their usual meanings. So the effect of PBS pH values on the surface coverage concentration $\acute{\Gamma}$ was investigated in a pH range of 5.5-8.3. As shown in Fig. 1 (a), the surface coverage concentration increased gradually with the increase of pH values in the range of 5.5-7.3 and reached a maximum value at pH 7.3. When pH value was above 7.3, the surface coverage concentration $\acute{\Gamma}$ began to decrease. However, the higher surface coverage concentration was found in 0.04 M PBS (Fig. 1 (b)). Thus, 0.04 M PBS (pH 7.4) was used to prepare poly-SP. The influence of SP concentration was tested in the range of 0.1-0.8 g$\cdot$$L^{-1}$ and the results were