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Electrochemical sensor for detecting both oxidizing and reducing compounds based on poly(ethyleneimine)/phosphotungstic acid multilayer film modified electrode

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ABSTRACT

A novel electrochemical sensor was prepared by alternatively deposition of anionic phosphotungstic acid (PTA) and polyelectrolyte poly(ethyleneimine) (PEI) on ITO glass through Layer-by-Layer assembly technique. Ascorbic acid and H_2O_2 were used as model drugs to investigate the electrocatalytic behavior of PEI/PTA multilayer film modified electrode in 0.1 M NaAc-HAc buffer (pH 5.0), respectively. The results showed that the corresponding current response of redox peak increased linearly with the increase of the concentration of them in certain ranges. The results of the standard addition method at three concentration levels testified that as-prepared electrode can be used to determine both of oxidizing and reducing compounds with low detection limits and high recoveries. And more, the response current of the electrode still can remain 96% of its initial activity after 100 cycles of CV scan. The PEI/PTA multilayer film modified electrode was further used to determine ascorbic acid in three commercially available fruit drinks, and the results were validated by high performance liquid chromatography, it was found that no statistically significant difference existed between the two methods. Compared with previous reports, the PEI/PTA multilayer film modified electrode can be used to determine both of oxidizing and reducing compounds with high sensitivity, good stability and reusability.

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1. Introduction

During the last decades, much research has been published describing various sensors, since the application of sensor is becoming more and more popular in various potential fields, such as biochemical field, electric system, medical diagnosis, environmental protection etc., depending on its advantages like small size, high sensitivity and stability, low-power, simultaneous detection multi-materials. However, novel functional material was still a challenge for the development and breakthrough the traditional sensor.

Due to their well-defined primary structure, high electronic density, special electrochemical properties and well water-solubility, polyoxometalates (POMs) have received much attention in electrochemical field [1–3]. As the simplest polyoxometalate, phosphotungstic acid (PTA) with Keggin structure has be proved to be an excellent electro-catalyst. A series of PTA based

electrochemical sensors had been prepared by immobilizing in solid silica material prepared by sol-gel chemistry [4], encapsulating in a metal organic framework [5], or grafting on magnetic nanoparticles [6] etc. Recently, PTA based composite film received increasing attention due to its simplicity and efficiently. Till now, it has been reported that PTA/Nafion, PTA/Graphene oxide, PTA/Poly (2,5-dimethoxyaniline) and PTA/Chitosan composite films were prepared based on electrodeposition [7], self-assembled monolayer [8], spray pyrolysis [9] and Langmuir-Blodgett techniques etc. [10], and all of them showed great electrocatalytic activities [11–14].

In recent years, Layer-by-Layer (LbL) self-assembly technique has emerged as a versatile and convenient method for the construction of thin films with precise control of film thickness and compositions, and has also been attracted to fabricate POMs multilayer films for applications in electrochemical field. For example, Lee group had successfully fabricated the PDPA/PTA multilayer film, which possessed a remarkable electrocatalytic activity towards oxidation of ascorbic acid (AA) [15]. Ma et al. had found that the $P_2W_{16}V_2$-AuPd/PEI multilayer film can electro-catalyze oxidation of dopamine [16]. Cox and his co-workers had reported that the PMo_{12}/PAMAM multilayer film exhibited

efficient catalysis oxidation of arsenite [17]. Meanwhile, Hao et al. found that the TMPyP/PMo$_{12}$ multilayer film displayed good electrocatalytic activities towards the reduction of BrO$_3^-$ [18]. The K$_7$P$_2$W$_{17}$O$_{61}$/QPVP-Os multilayer film fabricated by Li et al. could effectively catalyze the reduction of H$_2$O$_2$ [19], etc. In those works, POMs multilayer films played as electrochemical sensors to efficiently catalyze either oxidizing or reducing compounds along. However, POMs have both reducing and oxidizing properties, which meant they could act as electrochemical sensors to both of oxidizing and reducing reagents. Based on this view-point, a novel multilayer film modified electrode consisted of PTA and polyelec-trolyte poly(ethyleneimine) (PEI) was fabricated through LbL technique, and its reversible redox properties were fully utilized to determine the reducing or oxidizing reagents using AA or H$_2$O$_2$ as models, which resulted in a good linear relationship with the concentration of AA or hydrogen peroxide. The results confirmed our presumption that PEI/PTA LbL film could be used as electrochemical sensors for detection of both oxidizing and reducing substances.

2. Materials and methods

2.1. Materials

Poly(ethyleneimine) (PEI, M$_W$ 50,000, 50%) was obtained from Sigma-Aldrich (St. Louis, MO, USA) and used as received. Phosphotungstic acid (H$_3$PW$_{12}$O$_{40}$·XH$_2$O, PTA, M$_W$ 2880.3) was purchased from Tianjin Guangfu Fine Chemical Research Institute Co., Ltd. (Tianjin, China). Acetone, sulfuric acid (H$_2$SO$_4$, 98 wt%), hydrogen peroxide solution (H$_2$O$_2$, 30 wt%), sodium hydroxide (NaOH), acetic acid (HAc) and sodium acetate (NaAc) were all purchased from Tianjin Chemical Reagent Co., Ltd. (Tianjin, China). Ascorbic acid (AA) was obtained from Tianjin Baishi Chemical Co., Ltd. (Tianjin, China). All other chemicals were analytical grade and used without further purification.

2.2. Film preparation

Briefly, a substrate (quartz slide or indium tin oxide (ITO) glass, 1×5 cm^2 in size) was cleaned according to literates [20,21] as followed. Quartz slides were cleaned by treatment with Piranha solution (H$_2$O$_2$ (30%)/H$_2$SO$_4$ (98%) = 1/3, v/v) for 30 min followed by rinsing with deionized water and dried under a stream of air. ITO substrates were cleaned by immersing them into acetone solution under ultrasonic cleaning, and then immersed in concentrated sodium hydroxide solution under ultrasonic cleaning for certain

time, followed by thoroughly washing with deionized water. After the cleaning step, the substrate was immersed in PEI solution for certain time and followed by rinsing with water and dried under air. The PEI-coated substrate was then immersed into PTA solution for certain time also followed by rinsing and dried under air. After trial and error, the optimized conditions were 500 mg/mL PTA for 5 min or 2 wt% PEI solution for 5 min, respectively. This procedure was repeated as many times as the number of bilayers expected, which can be expressed as (PEI/PTA)$_n$, where n is the number of bilayers. The process of experiment was finished in air atmosphere at room temperature (20 ± 2 °C).

2.3. Instrumentation and measurements

Ultraviolet-visible spectrophotometer (UV–vis, T6, Beijing Purkinje General Instrument Co., Ltd., China) was used to monitored the growth process of the multilayer film. Fourier transform infrared (FT-IR) spectra were recorded in the range of 600–2000 cm^{-1} using IR Vertex 70 spectrometer (Bruker, Germany). An energy dispersive spectroscopy analyzer (EDS, 2000 Oxford Link ISIS-2000) was used for local elemental composition determination. To study electrochemical behavior of the PEI/PTA multilayer film, an electrochemical workstation (CHI 660C, Shanghai Chenhua Instrument Factory, China) was used with a conventional three-electrode system, including PEI/PTA multilayer film coated ITO electrode as working electrode, together with a calomel and a platinum as reference and counter electrode, respectively. Cyclic voltammetry experiments were carried out at a scan rate of 50 mV/s over the relevant potential range using a 0.1 M NaAc-HAc buffer (pH 5.0).

3. Results and discussion

3.1. Fabrication of the multilayer films

The LbL self-assembly of cationic PEI and anionic PTA onto the negative surface of the film basically depended upon the electrostatic attraction between the oppositely charged species. The growth process of the multilayer films was monitored by UV–vis absorption spectroscopy. Absorption curves of PEI and PTA solutions were firstly determined and results was illustrated in Fig 1(A). It can be observed that PEI solution showed no absorption above 200 nm (Fig. 1(A,b)), and PTA solution had the characteristic absorption peak at 268 nm (Fig. 1(A, a)). Fig. 1(B) showed the adsorption profiles of PEI/PTA films with different number of bilayer. As shown in the inset of Fig. 1(B), an obvious linear
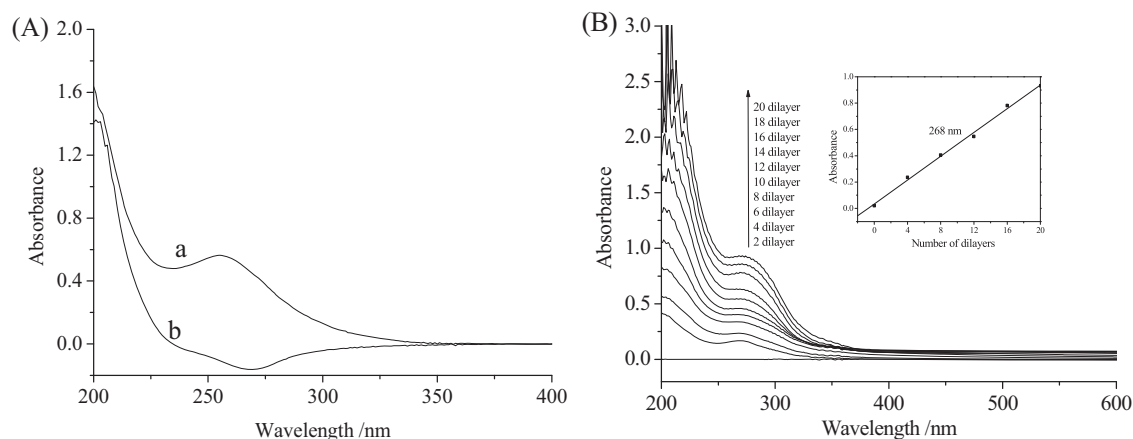

Fig. 1. UV–vis spectra of (A, a) PTA aqueous solution; (A, b) PEI aqueous solution; and (B) (PEI/PTA) n multilayer films with n = 0–20 bilayers on quartz substrate. The inset shows plots of the absorbance values at 268 nm as a function of the number of deposition bilayers.