



Studies on the electrocatalytic oxidation of dopamine at phosphotungstic acid–ZnO spun fiber-modified electrode

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ABSTRACT

A novel and selective electrochemical sensor was developed for the determination of dopamine (DA) based on phosphotungstic acid (PWA)–zinc oxide (ZnO) electrospun fibers. The fibers were constructed in situ on a Pt electrode by using electrospinning technology and succeeded heat treatment. The obtained fibers were characterized by SEM, FTIR, and XRD. The electrochemical properties of PWA–ZnO fibers modified electrode and its electrocatalysis for DA electro-oxidation were investigated by cyclic voltammetry and differential pulse voltammetry. The stability of PWA–ZnO fibers was excellent because PWA was embedded in the fibers, which can solve the problem of PWA loss during experiment. According to large surface area of PWA doped ZnO fibers, the modified electrode showed excellent electrocatalytic activity toward the oxidation of DA in the phosphate buffer solution (pH 5.0). A linear relationship between the current response and the concentration of DA ranging from 1.9×10^{-7} to 4.5×10^{-4} M was obtained with a detection limit of 0.089 μ M at pH 5.0. The DA can be determined in the presence of ascorbic acid (AA) because two compounds were well-separated with a potential difference of 0.36 V on the modified electrode. Based on its excellent electrochemical performance and ease of preparation, the proposed electrode may provide a promising alternative in routine sensing applications.

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1. Introduction

Electrochemical sensing technique has been recognized as one of efficient methods for the determination of target compounds due to its characteristics of high sensitivity, fast response, easy miniaturization and integration [1,2]. Biomaterials modified electrodes have gained special focus based on their advantage of excellent selectivity in recent decades [3]. Unfortunately, these biomaterials, such as enzyme and antibody, were not favorable for long-term detection owing to their inherent disadvantage, e.g. poor stability, short life span. Moreover, high price of these biomaterials also limited their applications [4]. To overcome these drawbacks, considerable efforts have been oriented to construction of electrochemical sensors based on developing novel electroactive materials with good catalytic activity and stability. Quite a number of important achievements were obtained, such as the non-enzymatic glucose sensor based on various nanoscale semiconducting metal oxides [5–7].

Heteropoly acids (HPAs) have been investigated extensively on both fundamental research and technical applications because of their remarkable catalytic performance and stability [8,9].

Recently, researchers found that the redox potential of HPAs could be modulated by regulating heteroatom or coordination atom on HPAs structure according to application requirements. The design and synthesis of novel HPAs has become a hotspot in recent years. These prominent characteristics make HPAs a good candidate to serve as catalysts and construct highly sensitive electrochemical sensors. Various techniques including electro-deposition [10], self-assembly [11], and electrostatic absorption [12] have been developed to immobilize HPAs on electrodes surface. However, Ramesh Kumar et al. [13] stated that the major disadvantages of HPAs as a material for electrode modification lie in the low surface area and high solubility in experiment, which reduces sensitivity and stability of these electrodes in analytical application. Some methods have been adopted to solve these problems, such as loading HPAs on nano-materials surface. Maiyalagan [14] has prepared silicotungstic acid/Pt–Ru nanoparticles and used this material to construct an electrochemical sensor for the detection of methanol. Unfortunately, nanoparticles with large surface energy were prone to aggregate during immobilization of them on electrode surface, which reduced the electro-active area of HPAs and sensitivity of the sensor for determination of target molecules. One-dimensional micro/nanofibres membrane with reticular structure may be one of suitable materials for immobilization of HPAs, which not only improve the catalytic activity of HPAs-modified nanofibres but also sort out the problem of agglomeration. To the best of our

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knowledge, there were few literatures using micro/nanofibres membrane as supporter for immobilization of HPAs. Electrospinning has recently been reported as a convenient and effective technology for fabricate micro/nanofibres [15]. The obtained fibers exhibited peculiar and fascinating electrochemical performances because of large surface-to-volume ratios and its reticular structure [16]. In this research, phosphotungstic acid (PWA) was selected to be a model HPAs for construction of composite fibers by incorporating it into electrospinning fibers, and the composite fibers was then employed as electro-active material to fabricate a electrochemical sensor.

Dopamine (DA) is a ubiquitous neurotransmitter molecule of catecholamines in mammalian brain tissues, and a decrease in its concentration would be related with brain disorders such as Schizophrenia, Parkinson's disease, and HIV infection [17,18]. The determination of DA plays an important role in various research areas such as the neurophysiology, the quality of medicines, and the mechanism of medicines. Since there are many publications about the determination of DA, in this research, DA was chosen as a target material to estimate the availability of the PWA doping electrospinning fibers modified electrode by comparing with DA sensors that electrodes were modified with other electro-active materials.

In this paper, a novel PWA–ZnO fibers modified electrode was fabricated by using electrospinning technique for the determination of DA in the presence of ascorbic acid (AA). The morphology and structure of obtained fibers were characterized by scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and X-ray powder diffraction (XRD). The direct electrochemical behavior of PWA–ZnO fibers membrane modified Pt (PWA–ZnO/Pt) electrode was studied for the first time. The electrocatalytic oxidation of DA on PWA–ZnO/Pt electrode was also investigated using differential pulse voltammetry. Results obtained with the PWA–ZnO modified electrode are presented in this paper and discussed in detail.

2. Experimental

2.1. Chemicals and reagents

DA was obtained from Sigma (>99.0%). DA hydrochloride injection solution was obtained from Wuhan Grand Pharmaceutical Group Co., Ltd. (Wuhan, China). AA, acetic acid, zinc acetate [Zn(Ac)₂], PWA and poly(vinyl alcohol) (PVA, degree of polymerization = 1750 ± 50, degree of hydrolysis = 98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Phosphate-buffered solutions (PBS) were prepared from stock solution of 0.1 M K₂HPO₄ and 0.1 M KH₂PO₄. All reagents were of analytical grade or better. Highly pure Pt wire with diameter of 1.0 mm and working length of 3.0 cm was used to construct working electrode. The electrode area is about 0.094 cm². Double distilled water was used for all experiments.

2.2. Instrumentation

During electrospinning, a high-voltage power (ES30P-5w/DDP; Suzhou, China) was applied to polymer in a syringe (781101; KD Scientific, USA) through an alligator clip attached to the syringe needle. Thermal treatment was performed using a muffle furnace (GSL-1300X; Hefei, China). The obtained fibers were characterized using an SEM system (KYKY2800, China) at an accelerating voltage of 15.0 kV, an FTIR system (NICOLET 380, Thermo, USA) using KBr pellets and an XRD Analyzer (Shimadzu XRD 6000, Japan).

Voltammetric experiments, such as cyclic voltammetry (CV) and differential pulse voltammetry (DPV), were performed with a CHI 660C electrochemical analyzer (Chenhua, Shanghai, China)

using a personal computer to control measurements and treat data. The standard three-electrode system consisted of a platinum sheet as the auxiliary electrode, a saturated calomel electrode as the reference electrode, and the PWA–ZnO/Pt electrode as the working electrode (Φ 0.1 cm × 3 cm). After each experiment, the PWA–ZnO/Pt electrode was washed in 50 mL PBS buffer (pH 5.0) thoroughly and used for next examination. All measurements were conducted at room temperature (25 °C ± 1 °C).

2.3. Fabrication of PWA–ZnO/Pt electrode

The precursor solution was prepared according to the following steps. First, PVA (9%, w/v) colloidal solution was prepared by dissolving 2.7 g PVA grains in 30 mL acetic acid (2%, v/v) at 90 °C with 4 h continuous stirring. Then, 1.2 g PWA and 1.2 g Zn(Ac)₂ were added into 10 mL distilled water, and the solution was sonicated for 10 min to dissolve the grains completely. Finally, the obtained solution was added into the PVA solution, and the mixture was stirred for 2 h and kept in a water bath maintained at 50 °C to form a homogeneous and viscous precursor solution. Before modification, the bare Pt electrode was well polished with aqueous slurries of alumina powder (0.05 μm), rinsed, ultrasonicated in double distilled water, and dried under a stream of high purity nitrogen and ready for use.

The as-prepared precursor solution was loaded into a syringe and connected to the high-voltage power supply. Several key operational parameters, such as the flow rate, collection distance, and applied potential, were examined and optimized according to the morphology of obtained fibers. In brief, 20.0 kV of voltage was applied to the syringe needle and collector. The precursor solution was delivered to the blunt needle tip via syringe pump to control flow rate of 5 μL/min. The collection distance between the syringe tip and collector was 20 cm. Under the above fixed electrospinning conditions, the acquisition time of fibers was about 30 to obtain sufficiently thick membrane on the surface of Pt electrode that was connected to the collector. After electrospinning and air drying, the obtained fibers modified electrode was treatment at 80 °C for 10 h. Then, the electrode was calcined for 2 h at 400 °C at a heating rate of 5 °C/min under air atmosphere.

3. Results and discussion

3.1. Characteristics of PWA–ZnO fibers

The morphologies of as-prepared uncalcined and calcined composite fibers were examined by SEM and shown in Fig. 1. Uniform and continuous PWA–Zn(Ac)₂–PVA fibers were obtained from electrospinning (Fig. 1A). After calcinations of the obtained fibers, a PWA–ZnO fibers membrane was formed with a decrease of its average diameter (Fig. 1B). This phenomenon could be attributed to the elimination of PVA and the decomposition of Zn(Ac)₂. The structure of the fibers membrane was reticular, which improved the fibers' inflexibility and provided even a larger accessible surface area for the subsequent electrochemical catalytic oxidation of target molecules.

FTIR spectra were used to characterize the loading of PWA into ZnO fibers and shown in Fig. 2. The fibers membrane was powdered and mixed with KBr. The intense band at 520.9 cm⁻¹ may be assigned to the Zn–O stretching (Fig. 2 (curve a)), indicating that Zn(Ac)₂ had been converted into ZnO by calcination. The fundamental vibrational modes of the PWA Keggin cluster structure were demonstrated in Fig. 2 (curve b). The peaks at 1081.1, 980.8, 892.0, and 819.8 cm⁻¹ can be attributed to the stretching vibrations of P–O_a, W=O_t terminal oxygen atoms, W–O_b–W oxygen-bridges, and W–O_c–W oxygen-bridges, respectively, related to the Keggin

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