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Strong adsorption characteristics of a novel overoxidized poly(3,4-ethylenedioxythiophene) film and application for dopamine sensing

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ABSTRACT

An overoxidized poly(3,4-ethylenedioxythiophene) film-modified screen-printed carbon electrodes (SPCE/PEDOT$_{ox}$) was prepared and characterized by field emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS) and water contact angle techniques. The obtained film is a porous structure with highly abundant oxygen functionality. The SPCE/PEDOT$_{ox}$ could adsorb cations strongly and perform catalytic oxidation of biomolecules. The potential-induced adsorption of dopamine was observed for SPCE/PEDOT$_{ox}$. A simple medium-exchange procedure was developed for the selective determination of dopamine by the use of the dopamine-adsorbed electrode. Under optimal differential pulse voltammetry (DPV), the proposed assay can be employed in the determination of submicromolar concentration of dopamine without the coexisting interferences of ascorbic acid (1000-fold) and uric acid (10-fold).

1. Introduction

Fast and reliable electrochemical biomolecule sensors have been extensively developed due to the rapidness, high sensitivity, easy operation, low cost and the ability of in vivo sensing [1]. Dopamine (DA) is an important neurotransmitter for message transfer in the central nervous system [2], and reports have indicated that the lack of DA could cause brain disorders such as schizophrenia and Parkinson's disease [3]. The electrochemical determination of DA is a facile approach by the direct oxidation at conventional electrodes. However, the primary problems for the monitoring DA in body fluids and extracelluar fluid are the very low DA concentration co-existed with extremely high concentration of interference of ascorbic acid (AA) and uric acid (UA) (100–1000X excess) [4,5]. Besides, the oxidation potentials of AA, DA, and UA usually overlap at conventional electrodes [6], leading to low selectivity and inaccurate determination. Therefore, researchers have dedicated to design novel materials such as conducting polymers [2–4], carbon materials [3–7] and electrocatalysts [5], solely or in hybrids, for the convenient and accurate detection of DA alone or in the presence of AA and UA [1–7].

As a DA electrochemical sensor, good sensitivity and high selectivity are the key demands. Modification of electrodes with novel materials has been successful to improve the analytical performance of DA [1–7]. In order to improve the detection selectivity, there were efforts mainly focused on the separation of the oxidation peaks of AA, DA and UA by the use of suitable modified materials [1–3,5]. Inhibiting the interferences from reaching the sensing surfaces has been considered an effective way to improve DA detection. In this regards, preventing anionic AA and UA with a permselective Nafion film [4] and negatively charge carbon dots [6,7] was investigated, and the obtained electrochemical signals relied on oxidation of DA itself. However, the test solutions contained AA and UA in the ranges of 1–150X excess of DA. In order to application to the physiological samples, it is still worthy to investigate new materials for DA assays in the presence of very high amounts of interference AA and UA.

Literatures have indicated that conducting polymers in different overoxidation states showed unique features useful for analytical applications [8–13]. The treated conducting polymers are known as overoxidized films. Reports have shown that overoxidized polypyrrole [9–12] and overoxidized polyimidazole [13] were featured as insulating films with low background current. Overoxidation is an irreversible degradation reaction, and the experimental conditions have a great effect upon the property of the obtained products. In the presence of high concentration of powerful oxidants, the prepared conducting polymers, such as

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polypyrrole (PPY) and poly(3,4-ethylenedioxythiophene) (PEDOT), showed low electronic conductivity [8]. A high-potential or cyclic potential treatment of PPY in various types of electrolyte solutions [9–12] also resulted in the alteration of the electronic and electrochemical properties, including reduction of background current and loss of electrical conductivity [12,14]. Reports indicated that the overoxidized PPY film (PPY_{ox}) showed a rough surface with micro-sized pores [10,11,14]. Pereira et al. observed the suppression of anion insertion (intercalation) in the PPY_{ox} matrix [14]. They also observed a mass loss [14], consistent with the dedoped state of the PPY_{ox} film [15]. The analytical aspects of the PPY_{ox}, regarding to the film permselectivity to ionic probes, have been investigated [9–12]. Reports showed small apparent diffusion coefficients for anionic $Fe(CN)_6{}^{3-}$ and 3,4-dihydroxyphenylacetate [16] and weak oxidation current response for cationic dopamine and serotonin [11] at the PPY_{ox}-modified electrodes. Therefore, PPY_{ox} usually combined with the other materials to form composites for the determination of catecholamine neutrotransmitters [9–11].

Here, we propose a novel DA assay based on the overoxidized conducting polymer, and to some extent solve the interference problems from very high excess of AA. PEDOT is a stable conducting polymer because of the 3,4-ethylenedioxy group, and has been used to recognize small molecules [2,17]. Researchers have studied the structure morphology and physical/chemical properties of the overoxidized PEDOT film ($PEDOT_{ox}$) [8,18–20], however, the usage of $PEDOT_{ox}$ in electroanalytical applications is rarely reported. In this study, the degradation extent of PEDOT was properly controlled by the potentiostatic conditions in order to explore the sensing ability for DA. The obtained $PEDOT_{ox}$ film showed apparently unique characteristics, including the electrical conductivity and recognition of inorganic and organic chemicals. Due to the remarkable adsorption characteristics of $PEDOT_{ox}$ towards DA, we developed an electrochemical assay for the submicromolar determination of DA without the interferences of 1000X excess of AA and 10X excess of UA under the physiological conditions. The sensing approach combines the potential-induced strong affinity of DA to $PEDOT_{ox}$ and the benefit of medium-exchange from the mixture solutions to a blank buffer solution, where the direct oxidation of the adsorbed targets by differential pulse voltammetry were recorded. The anionic AA was not adsorbed by $PEDOT_{ox}$, therefore, its related interferences were avoided. UA showed adsorption onto $PEDOT_{ox}$, however, its oxidation potential was well separated from that of DA, and did not cause interference problems.

2. Experimental

2.1. Reagents

3,4-Ethylenedioxythiophene (EDOT) was obtained from Aldrich. Ascorbic acid, dopamine, uric acid and hydroxypropyl-β-cyclodextrin (HP-β-CD) were obtained from Acros. These chemicals were of the highest available grade and used without further purification. All other chemicals were of analytical reagent grade and also obtained from Acros. The 0.1 M, pH 7.0 phosphate buffer solutions (PBS) was prepared using de-ionized water from a Milli-Q ultrapure water system with a resistivity of 18 MΩ cm.

2.2. Instruments

Electrochemical experiments were performed with a voltammetric analyzer (CHI, model 621C and 6116E). A bare screen-printed carbon electrode (SPCE, geometric area 0.2 cm^2) from Zensor R&D (Taiwan) was employed as the working electrode and used without pretreatment. A platinum wire and a homemade Ag|AgCl|KCl (sat.) were used as counter and reference electrode, respectively. All potentials were reported with respect to this reference electrode. The voltammograms were plotted with increasing positive potential to the right and anodic (positive)

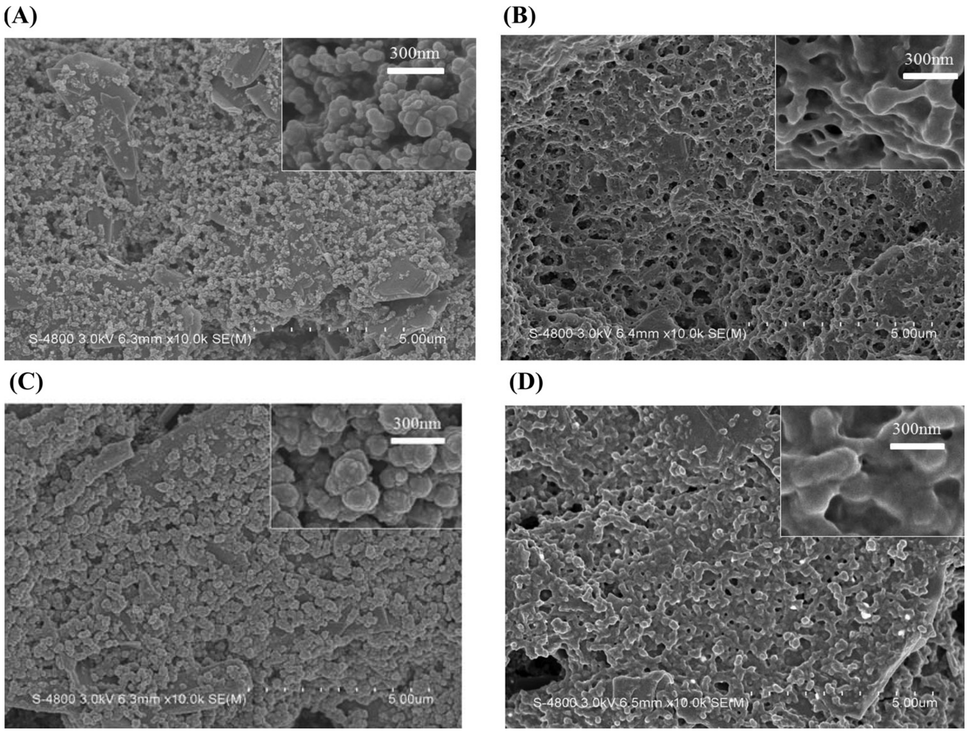

Fig. 1. Scanning electron micrographs of (A) bare SPCE (B) SPCE* (C) SPCE/PEDOT (D) SPCE/$PEDOT_{ox}$.