



Selective detection of L-tyrosine in the presence of ascorbic acid, dopamine, and uric acid at poly(thionine)-modified glassy carbon electrode



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ABSTRACT

A simple, sensitive, and selective electrochemical sensor for the detection of L-tyrosine (Tyr) in the presence of ascorbic acid (AA), dopamine (DA), and uric acid (UA) at physiological pH in phosphate buffer solution (PBS) was developed based on a poly(thionine)-modified anodized glassy carbon electrode (PTH/AGCE). The PTH/AGCE resolved the voltammetric signals of AA, DA, UA, and Tyr with peak potential separations (ΔE_p) of ca. 157, 135, and 325 mV between AA–DA, DA–UA, and UA–Tyr, respectively, with high sensitivity. The bare GCE and anodized GCE also resolved the Tyr oxidation signals from the interferents but the sensitivity was quite low. The PTH/AGCE sensor exhibited excellent selectivity towards Tyr detection in the presence of higher concentrations of AA, DA, and UA. The differential current responses increased linearly with increasing Tyr concentration in the range of 1 to 250 μM . The sensitivity and detection limit ($S/N = 3$) were found to be 1.05 $\mu\text{A}/\text{cm}^2/\mu\text{M}$ and 0.57 μM , respectively. The sensor exhibited excellent stability and reproducibility and could detect the Tyr concentration in human serum samples with excellent recoveries.

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1. Introduction

Tyrosine (Tyr) or 4-hydroxyphenylalanine is familiar as a non-essential aromatic amino acid synthesized from phenylalanine and incorporated into proteins in human and herbivore bodies [1,2]. It is a basic constituent of proteins and is vital for establishing and maintaining a positive nitrogen balance in the human body [3]. Sometimes it is also added to dietary and food products and to pharmaceutical formulations because of its minimal presence in vegetables. It is a vital precursor of several neurotransmitters in the mammalian central nervous system, including L-dopa, dopamine (DA), norepinephrine, and epinephrine [4,5]. A low level of Tyr could cause albinism and alkaptonuria [6], whereas a high level induces Parkinson's disease, depression, and mood disorders [7,8]. Alteration of Tyr concentration is related to several other diseases such as atherosclerosis and lung diseases [9]. It is well known that ascorbic acid (AA), DA, and uric acid (UA) usually co-exist with Tyr in biological fluids and the oxidation potentials of these substances are close to the oxidation potential of Tyr [10]. Therefore, the selective and rapid detection of Tyr in the presence of AA, DA, and UA in human blood serum, blood plasma, and urine is pharmacologically very important.

Several methods have been employed to determine the concentration of Tyr, including chromatography, spectrophotometry, spectrofluorimetry, *etc.* [11–15]. Most of these conventional methods are very tedious, dependent on multi-step sample clean-up procedures, relatively expensive, and time consuming. On the contrary, electrochemical detection methods are much more advantageous in terms of sensitivity, selectivity, and simplicity [16–19]. Various electrode modifiers such as conducting polymers (CPs), butyrylcholine (BuCh), and multi-wall carbon nanotubes (MWCNTs) have been utilized to enhance the sensitivity of interference-free Tyr detection [20–22]. Among them, CP films are known to be one of the most effective materials for surface modification owing to their ease of preparation, strong adherence to the substrate, excellent chemical stability, and good conductivity [16,19]. In particular, poly(thionine) (PTH) is a potential CP that can be easily synthesized and electrochemically deposited from thionine on glassy carbon electrode (GCE) and Au electrode surfaces [16,19]. PTH-modified electrodes such as PTH/GCE and PTH/Au have already been used for various electrochemical sensing applications, which include DA [23], UA [23], dihydronicotinamide adenine dinucleotide (NADH) [24], DNA hybridization [25], glucose [26], and H_2O_2 [27]. It is well established that PTH-modified anodized GCEs can easily separate the oxidation signals of AA, DA, and UA, whereas bare GCEs cannot. One report mentions the detection of Tyr in the presence of AA and UA based on a 3-amino-5-mercapto-1,2,4-triazole (p-AMTa)-modified GCE [10]. To the best

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of our knowledge, no report is available for the selective detection of Tyr in the presence of AA, DA, and UA.

In this paper, we report a poly(thionine)-modified anodized glassy carbon electrode (PTH/AGCE) for the selective detection of Tyr in the presence of AA, DA, and UA. It was found that the PTH film possessed excellent electrocatalytic activity towards the oxidation of Tyr. The PTH/AGCE sensor selectively detected Tyr with excellent signal sensitivity without interference from AA, DA, and UA. Various experimental parameters such as the variation of the number of voltammetric cycles for PTH deposition and the pH were optimized to obtain the desired increased sensitivity and selectivity for Tyr detection.

2. Experimental

2.1. Chemicals

Double-distilled water obtained from a Milli-Q water-purifying system ($18 \text{ M}\Omega \cdot \text{cm}$) was used throughout the experiments unless specified otherwise. Thionine acetate (dye content, ~95%), L-tyrosine, dopamine hydrochloride (DA), uric acid (UA), L-ascorbic acid (AA), disodium hydrogen phosphate (Na_2HPO_4), and sodium dihydrogen phosphate (NaH_2PO_4) were purchased from Sigma-Aldrich (St. Louis, MO). Phosphate buffer saline (PBS) solution was prepared by mixing 0.1 M Na_2HPO_4 with 0.1 M NaH_2PO_4 . All the experiments were carried out at room temperature.

2.2. Instrumentation

Electrochemical experiments were performed using a CHI430A electrochemical workstation (CH Instruments, Inc., USA). A conventional three-electrode system was used, in which a bare GCE (3 mm diameter, electroactive surface area of ca. 0.07 cm^2), AGCE, or PTH/AGCE was used as the working electrode. A platinum (Pt) wire and Ag/AgCl (aq. saturated KCl) were used as the counter and reference electrodes, respectively. All potentials in this study referred to this reference electrode. Differential pulse voltammograms (DPVs) were obtained by scanning the potential with the following: pulse amplitude, 100 mV/s; pulse width, 2 ms; and pulse period, 1000 ms. All electrochemical experiments were performed in 0.1 M PBS.

The surface topography of the electrodes was investigated by atomic force microscopy (AFM, XE100, PSIA, Korea) in non-contact mode. All the AFM measurements were performed with a XE scan system with the scan size of $1 \mu\text{m}$ in x–y. Silicon type PPP-NCHR non-contact cantilever with $125 \mu\text{m}$ length, 42 N/m force constant, and 330 kHz resonant frequencies were used. All images were taken at room temperature, scan rates 2 s^{-1} . The contrast and brightness of the images were adjusted and the background slope was removed by flattening. All images were visualized in three dimensions using the scanning probe image processor (Park SmartScan, Korea).

2.3. Preparation of the PTH/AGCE

Prior the electrochemical polymerization of thionine, the GCE was polished with a 0.05 mm alumina/water slurry on a polishing cloth (Buehler, Germany) to a mirror-like finish, followed by sonication and washing with distilled water. The electrochemical polymerization of thionine was conducted according to our previously reported protocol [23]. Briefly, the GCE was anodized by applying a constant potential (+1.8 V) for 400 s in PBS (pH 7.0), followed by the polymerization of thionine by sweeping the potential in 0.5 mM thionine solution (in PBS, pH 7.0) in the potential range of -0.4 to 0.1 V (Fig. S1). The resulting shiny, deep violet-blue film of PTH was very stable, and it was difficult to remove it from the surface unless the electrode was heavily polished.

3. Results and discussion

3.1. AFM characterization of the GCE, AGCE, and PTH/AGCE

Fig. 1 shows the AFM images of the GCE, AGCE, and PTH/AGCE. The AFM images clearly indicate that the anodization process increased the roughness of the GCE from ca. 0.95 to 1.932 nm via the introduction of three-dimensional oxidized graphitic particles with an average particle diameter of ca. 50 nm [28]. The anodization process induced an increase in the number of oxygen-containing functional groups (e.g. $-\text{COOH}$, $-\text{CO}-$, $-\text{CHO}$, etc.) on the GCE surface, which facilitated thionine-free radical formation and adsorption onto the AGCE and the subsequent formation of a PTH film [28,29]. A uniform PTH-particle film with an average particle size of ca. 75 nm and a roughness of ca. 1.914 nm covered the AGCE surface, which is consistent with the results previously reported [27].

3.2. Electrochemical behavior of Tyr at the GCE, AGCE, and PTH/AGCE

The PTH film deposited over 15 CV cycles at pH 7.0 (PBS) was chosen for the initial electrochemical characterization of Tyr. Fig. 2 shows the CV and DPV responses of Tyr (1 mM) at the GCE, AGCE, and PTH/AGCE. The CVs demonstrated that both the GCE and AGCE oxidized Tyr with low oxidation peak currents, with peaks at ca. 0.91 and 0.93 V, respectively, whereas the PTH/AGCE showed significant enhancement of the Tyr oxidation peak current, with peaks at ca. 0.82 V. The lower oxidation peak current and the positively shifted oxidation peak potentials for Tyr at the GCE are attributable to the adsorption of the oxidized Tyr onto the GCE surface [10]. On the other hand, the AGCE showed a lower oxidation current and more positively shifted oxidation peak potentials of Tyr as compared with GCE, which can be attributed to the strong electrostatic repulsion between the negatively charged AGCE and the negatively charged Tyr at pH 7.0. The PTH/AGCE showed enhanced sensitivity, with a more negatively shifted oxidation peak potential for Tyr as compared to GCE and AGCE, which

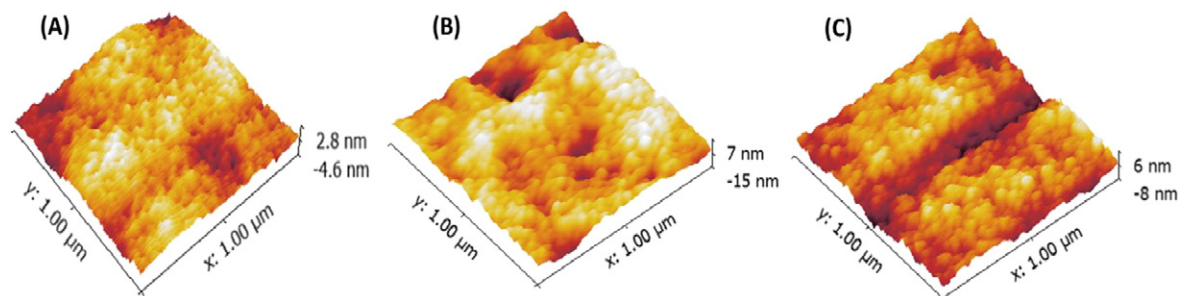


Fig. 1. Tapping-mode AFM images of (A) glassy carbon electrode (GCE), (B) anodized glassy carbon electrode (AGCE), and (C) poly(thionine)-modified anodized glassy carbon electrode (PTH/AGCE).

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