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Electrochemical preparation of polymeric films of pyronin Y and its electrolcatalytic properties for amperometric detection of nitrite

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ABSTRACT

Electropolymerization of pyronin Y (PyY) on pencil graphite electrode (PGE) was performed by using potentiodynamic and potentiostatic techniques. Effect of electrooxidation potential, pH, and concentration of monomer solution on the polymeric film structure was also investigated. Characterization of poly(PyY) thin films was carried out by using cyclic voltammetry, chronoamperometry, UV–Vis. absorption spectroscopy, and scanning tunneling microscopy. Electrocatalytical properties of prepared poly(PyY)/PGE were studied for amperometric detection of nitrite. Under optimized conditions, amperometric response of the poly(PyY) modified electrode was linearly proportional to the concentration of nitrite in the range from 1.0×10^{-6} to 1.0×10^{-4} M, with a detection limit of 5.0×10^{-7} M. The results indicate that the poly(PyY)/PGE exhibits a low detection limit, an acceptable linear range and a very high sensitivity. The modified electrode was tested for the amperometric determination of nitrite concentration in food samples and the results were consistent with those of the standard spectrophotometric method.

1. Introduction

Nitrite (NO_2^-) commonly exists in natural environment and is widely used as additive and corrosion inhibitor in food technology. The importance of quantitative determination of nitrite in water, food and agricultural products has been widely recognized because of it is found that nitrite can react with secondary amine to produce nitrosamine, which is a strong carcinogen to human bodies. Nitrosamines become highly reactive at the cellular level, which then alters gene expression and causes DNA damage. Therefore, quantitative detection and determination of nitrite is very important in analytical chemistry. Several methods have been employed for nitrite determination including spectrophotometric [1], chromatographic [2], and electrochemical methods [3]. Owing to high sensitivity, relatively good selectivity, fast response, simple use, and low cost, electrochemical techniques are favorable for nitrite determination. Electrochemical determination based on the oxidation of nitrite offers several advantages, especially no interference from nitrate ion and molecular oxygen.

Several conductive or semiconductive electrodes have been performed for amperometric determination of nitrite [4–6]. Pencil graphite electrode (PGE) is widely preferred as working electrode for electrochemical studies due to relatively large anodic potential window, low cost, stability, and adjustable active surface. Moreover, disposable PGEs have good mechanical rigidity and can be easily modified and miniaturized. PGEs are also suitable electrodes for trace analysis when it is used in combination with sensitive voltammetric techniques [7]. Since the nitrite oxidation involves a large overpotential, the usefulness of this approach is limited at bare electrodes. Thus, dye polymer thin film modified electrodes have been developed to decrease the overpotential for nitrite oxidation because surface of these modified electrodes introduces highly stable, electroactive, and efficient redox centers and provides a means of extending the dynamic range for analytical determination.

Modification of electrode surfaces by thin films of dyes can be achieved by using various techniques, e.g., self-quenching solution polymerization [8], incorporation into polymeric films or macromolecular deposits [9], supramolecular chain polymerization [10], chemical polymerization [11], and electropolymerization [12–19]. Electropolymerization is a powerful technique for development of dye polymer thin film modified electrodes. Among certain advantages of this technique, one should point out that the electropolymerization provides simplicity of targeting for selective modification of electrode. In addition, the electropolymerized materials usually possess some unique properties that are not peculiar to its corresponding monomer structure.

Pyronin Y (PyY), a water soluble xanthene derivative cationic dye, contains two tertiary amine groups in α position of xanthene ring [14]. Many advanced technologies, especially in electronic and optoelectronic devices, require thin layers of new functional

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materials with special optical, electrical, and surface properties. Xanthene dyes have high absorption coefficient and are easily processed and can be functionalized to obtain the specific optical and electrical properties. Owing to these properties, xanthene dyes are widely used, especially for dye lasers, solar energy conversion devices, photosensitizer compounds for chemical reactions, nonlinear optical media for many applications, and biosensor applications [14,15].

Monomer [20], dimer [21] or polymer [14–17] thin films of xanthene dyes have been prepared by using electrochemical techniques until now. Briefly, Kumar et al. have prepared poly(Pyronin B) thin film modified glassy carbon electrode (GCE) and they have applied to the electrocatalytic oxidation of reduced form of nicotinamide adenine dinucleotide (NADH) [15]. Zhang et al. have carried out electropolymerization studies of eosin Y in the presence of Zn^{2+} ions [16]. Thomas et al. have performed electropolymerization of rhodamine B on carbon paste electrode for detection of dopamine [17]. We have previously investigated nucleation and growth mechanism for polymeric film formation of pyronin Y from non-aqueous solutions on gold substrates by using cyclic voltammetry and chronoamperometry [14].

In this work, electropolymerization of PyY from aqueous solutions was investigated by using cyclic voltammetry, chronoamperometry, UV–Vis. absorption spectroscopy, and scanning tunneling microscopy. Effect of pH, monomer concentration, and electrooxidation potential on the electropolymerization process was determined. Electrocatalytical performance of poly(PyY) modified PGE was tested for amperometric detection of nitrite.

2. Experimental

2.1. Materials

Pyronin Y was purchased from Sigma Company and used as received. All other chemicals throughout this study were of reagent grade. Experiments were carried out in Milli-Q ultra-pure water (conductivity $5.5 \leqslant \mu S\ m^{-1}$). The temperature of the electrochemical cell was fixed at 30 °C by using a thermostat system to increase the dissolution of PyY. Phosphate buffer solutions (PBS, 0.1 M) of different pH values were prepared by mixing stock solutions of 0.1 M H_3PO_4 and KH_2PO_4, and the pH of the buffer solution was adjusted by using a Hanna pH-meter. 0.1 M H_2SO_4 solution used for pH 1.0 solution. Solution of 1.0×10^{-3} M $NaNO_2$ was prepared by directly dissolving sodium nitrite in buffer solutions. The solutions were deaerated by passing dry nitrogen through the electrochemical cell for 15 min prior to each experiment.

2.2. Electrochemistry

Electropolymerized thin films of PyY was prepared by using either cyclic voltammetry or constant potential techniques, with an Epsilon potentiostat system connected to a three electrode cell. In all cases, an Ag/AgCl (3 M NaCl) (Bioanalytical Systems) electrode served as reference electrode and a Pt wire was used as counter electrode. Different working electrodes were used for the synthesis and/or characterization of poly(PyY) films. Pencil graphite electrodes (PGEs) (Tombow 0.7 2B) were cleaned in ethanol by sonication for 10 min and then rinsed with doubly distilled water. The electrochemical activation of the surface of PGE was carried out by cyclic voltammetry between 0 and 1.6 V in pH: 7.0 PBS until reproducible electrochemical response was observed. PGEs were then washed with water and ethanol to remove the impurity and dried at room temperature before each experiment.

Morphological investigation of poly(PyY) thin films was performed on Au(111) single crystal substrates because it consists of an atomically flat surface [14]. Before the preparation procedure of Au(111) substrates, Au wires (Alfa Aesar, 99.999% purity) were cleaned by immersing in a bath of freshly prepared piranha solution (3:1 vol/vol of concentrated H_2SO_4/30% H_2O_2) for 5 min and then rinsed with doubly distilled water. Au(111) electrodes were prepared as described in Hammelin method [22]. Briefly, polycrystalline gold electrodes were flame-annealed in H_2 flame for about 30 s, and after a short time cooling in air, the electrodes were quenched in Milli-Q water. This procedure was repeated at least five times. After this process, a few large (111) facets form on polycrystalline surface. The dimensions of the facets may be as large as 1 mm and are visible by eye.

Indium tin oxide coated glass (ITO) electrodes (Sigma) with sheet resistance of $10\ \Omega\ cm^{-2}$ were used as working electrode for optical characterization of poly(PyY) thin films. ITO electrodes were cleaned by sonication in detergent solution for 5 min and then rinsed with a large amount of doubly distilled water. Further sonication in ethanol for 5 min was applied before being blown dry with a nitrogen stream.

2.3. Analytical procedure

Salami samples were collected from a local shop and pretreated according to following procedure. 5 g salami sample was beaten into mash was weighed and mixed with 12.5 ml of saturated borax solution while stirring. Afterwards, 300 ml water at 70 °C was added into the mixture and heated in boiling water for 15 min. 5 ml of 20% (w/w) zinc acetate solution was then added to precipitate proteins. After being cooled to room temperature, the mixture was diluted to 500 ml with ultra-pure water and placed quietly for a while. Followed gotten rid of the upper lipid layer, the clear solution was filtrated. Finally, 100 ml of the filtrate was concentrated to form a 10 ml solution. The resulting sample solution was stored at 4 °C in a refrigerator [23].

The nitrite content in food (salami) samples was determined by a conventional amperometric technique according to the standard additions method. Amperometric determination was applied on poly(PyY)/PGE at 930 mV in pH 4.0 media under stirring conditions (750 rpm). After the working electrode reached a steady baseline, the standard nitrite solution was added to electrochemical cell. Reference determination was performed by using spectrophotometric analysis method (Griess Assay) [23].

2.4. Instrumentation

Morphological investigation of poly(PyY) thin films was carried out in ambient conditions by using ex situ scanning tunneling microscopy (STM) technique with a Molecular Imaging model PicoScan instrument, USA. Pt–Ir (80:20) wire (Alfa Aesar) with a thickness of 0.2 mm was used as tunneling tips for STM imaging. Sharp tips were produced by cutting Pt–Ir wire with surgical scissors. UV–Vis. absorption spectra of poly(PyY) thin films on ITO electrodes were collected with a Shimadzu, Japan UV-3101PC UV–Vis.–NIR spectrophotometer.

3. Results and discussion

3.1. Cyclic voltammetry

Electropolymerization PyY was performed on PGE by using cyclic voltammetry. Proton concentration of monomer solution is very effective on the electropolymerization process of dyes [18,19]. Fig. 1 demonstrates 15 successive voltammetric curves of electropolymerization of PyY on PGE in the solutions of different pH values of 1.0, 3.0, and 5.0 containing 1.0 mM PyY. If potential