Journal of Molecular Liquids 211 (2015) 353–362

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Electrochemical characterization of poly(fuchsine acid) modified glassy carbon electrode and its application for simultaneous determination of ascorbic acid, epinephrine and uric acid

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ARTICLE INFO

Article history:
Received 3 March 2015
Received in revised form 23 June 2015
Accepted 10 July 2015
Available online xxxx

Keywords:
Fuchsine acid
Au nanoparticles
Ascorbic acid
Epinephrine
Uric acid

ABSTRACT

Electropolymerization of fuchsine acid (FA) was studied by cyclic voltammetry on the surface of a glassy carbon (GC) electrode in different electrolyte media. Then, a novel Au-nanoparticle poly-fuchsine acid film modified glassy carbon electrode (poly(FA)/AuNP/GCE) was constructed for the simultaneous determination of ascorbic acid (AA), epinephrine (EP) and uric acid (UA). The resulting poly(FA)/AuNP modified glassy carbon electrode was characterized by scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS) and reflectance Fourier transform infrared spectroscopy (ATR-FTIR). The poly(FA) film had an efficient electrocatalytic activity for the oxidation of AA, UA and EP, and decreased the charge transfer resistance of electrode. In addition, the poly(FA)/AuNP/GCE separate oxidation peak potential of AA–EP by 150 mV and EP–UA by 180 mV, while bare GCE fails to resolve them. Differential pulse voltammetry results exhibited linear dynamic range of 5.0–1120.0 μmol L^{-1} for AA, 0.5–792.7 μmol L^{-1} for EP and 2.85–650.2 μmol L^{-1} for UA with detection limits (S/N = 3) of 0.009 μmol L^{-1}, 0.01 μmol L^{-1}, and 0.03 μmol L^{-1} for AA, EP, and UA, respectively. The diffusion coefficient for the oxidation reaction of EP on AuNP/poly(FA) film coated GC electrode was calculated as $2.6(\pm 0.10) \times 10^{-5}$ cm^2 s^{-1}. The present method was applied to the determination of EP in pharmaceutical samples, AA in commercially available vitamin C tablet, and UA in urine samples.

1. Introduction

In recent years, electrochemically modified electrodes with conductive polymers or redox polymers have been widely used owing to their excellent unique physical and chemical properties [1–4]. They are the best approach for selective determination of some biomolecules because the surface characteristic on the electrode can be modulated by introducing various chemicals with a reactive group [5,6]. These polymer modified electrode show broad potential windows, and can catalyze some electrochemical reactions which have high overpotential and poor selectivity [7,8].

Carbon and metal electrode can be oxidized, and attach to various kinds of groups such as carboxyl, quinoidal and phenolic functionalities. Epinephrine, which is an important neurotransmitter in mammalians, has a group of mono-amines called catechol amine. Many diseases are related to the change of EP concentration in mammals. Thus, the determination of EP concentration is important in diagnosis and controlling medicine. The major problem for the determination of EP in vivo is the very low EP concentration and the large excess of interfering substances such as AA and UA [9]. Uric acid is produced in purine metabolism, and continuous monitoring of its concentration in body fluid is essential since concentration level abnormality is related to several diseases such as hyperuricemia, gout and kidney diseases [10,11]. Ascorbic acid is an effective agent in the human diet and it regulates the pH and antioxidant properties in the body. Electrochemical determination of AA, EP and UA is a promising candidate because they are chemically active. Furthermore, electrochemical methods have advantages such as simplicity, speed and sensitivity. EP is coexisting with AA and UA in biological fluids such as blood and urine, and the oxidation potentials of UA EP and AA are too close at bare electrode [8] leading to overlapping voltammetric signals. Therefore, it is important to develop the electrochemical technique for selective determination of EP in the presence of AA and UA.

The electropolymerization of monomers varies with experimental conditions such as media (acidic, neutral and slightly alkaline), solvent (organic and aqueous), substrate (gold, platinum, polished and activated GCE, screen printed carbon), and potential windows [12,13]. Fuchsine acid is a molecule with a three-branched sulfonate and an amine group. The poly(FA) on the surface of GCE has a high concentration of negative-charged function group $-SO^-_3$ and electron-rich nitrogen atoms. The electrochemical properties of poly(FA) films also depend on film preparation. For example, Chen and Chuang [14] have prepared poly(FA) glassy carbon electrodes by electrooxidative polymerization of

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http://dx.doi.org/10.1016/j.molliq.2015.07.029
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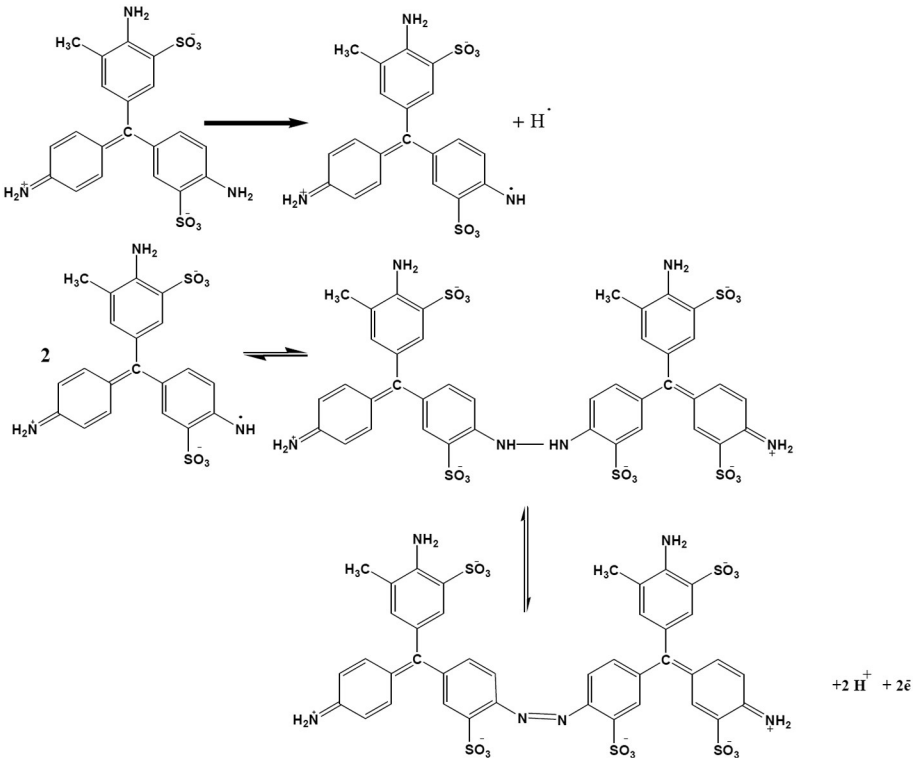

Scheme 1. Mechanism of electropolymerization of FA at GC electrode.

FA in pH 1.0. After polymerization, it forms a nano-sized monodispersed dendrimer film. The film formation process involves electron transfer from the monomer and polymer to the working electrode by consecutive cyclic voltammetry. We have used the poly(FA) film on activated GCE for the simultaneous determination of AA, EP and UA. We found that the electropolymerization of FA in acidic and neutral solution on the surface of electrode is not considerably more sensitive compared to the bare glassy carbon electrode for the determination of AA, EP and UA simultaneously. However, electropolymerization of FA in alkaline media shows good properties toward determination of AA, EP and UA, and incorporation of AuNPs on polymer modified electrode can extensively enhance the catalytic activity of glassy carbon electrode. This work illustrates that poly(FA)/AuNPs can not only catalyze oxidation of AA, EP and UA, but can also resolve their overlapped oxidation peaks efficiently. The proposed method is able to simultaneously determine these biomolecules in the urine sample and spiked samples in tablets.

2. Experimental

2.1. Apparatus and reagents

All electrochemical experiments including cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed using a Metrohm instrument, Model 797 VA processor. A conventional three-electrode electrochemical system was used for all electrochemical experiments, consisting of a working electrode (poly(FA)/AuNP/GCE modified glassy carbon electrode), a platinum wire counter electrode, and Ag/AgCl (3.0 mol L^{-1} KCl) as a reference electrode. A GCE with a formal surface area of 0.0314 cm^2 was used as the basal working electrode. All potentials reported are vs. Ag/AgCl.

A Corning pH-meter, Model 140, with a glass electrode (conjugated with an Ag/AgCl reference electrode, Model 6.0232.100) was used to determine the pH values of the solutions.

All chemicals used were of analytical grades, and doubly distilled water was used throughout. UA, fuchsine acid and EP were purchased from Sigma-Aldrich. AA was obtained from Merck. Stock solution of AA (0.010 mol L^{-1}) was prepared daily by dissolving a suitable amount of the reagent in water. UA solution (0.010 mol L^{-1}) was prepared by dissolving the solid in a small volume of 0.1 mol L^{-1} NaOH solution, and the solution was diluted with water to the desired concentration. Stock solution of EP (0.010 mol L^{-1}) was prepared daily by dissolving a suitable amount of EP in a small volume of 0.10 mol L^{-1} H_3PO_4 solution, and the resulting solution was diluted with water. Phosphate buffer solutions (PBS) with different pH levels were prepared by mixing 0.10 mol L^{-1} Na_2HPO_4 and 0.10 mol L^{-1} NaH_2PO_4 solutions at different ratios. The solution pH levels were adjusted by adding 1.0 mol L^{-1} H_3PO_4 and/or NaOH solution.

Other dilute standard solutions were prepared by appropriate dilution of the stock solutions in the phosphate buffer, pH 3.0.

2.2. Preparation of nano-gold poly-fuchsine-film modified glassy carbon electrode

Prior to modification, bare GCE was polished to a mirror finish using alumina slurries with 6, 1 and 0.05 μm. After each polishing, the electrode was ultrasonicated in ethanol and doubly distilled water for 5 min, successively, in order to remove any adsorbed substance on the surface. Finally, it was dried under nitrogen flow and was ready to use. The electrode was subsequently placed in a solution containing 0.005 mol L^{-1} fuchsine acid and 0.1 M NaOH solution and cyclic potential sweep was applied in the potential range of 0 to + 1.3 V for 25 cycles at 100 mV s^{-1}. Then, the electrode was rinsed and immersed into 0.4 g L^{-1} $HAuCl_4$ and 0.1 mol L^{-1} KNO_3 to electrodeposit AuNPs for 60 s at − 0.2 V [24]. The resulting electrode, poly(FA)/AuNP/GCE, was activated by several cyclic voltammetries in potential range between − 0.5 and 1.0 with a scan rate of 100 mV s^{-1} in a buffer solution (pH 3.0) until a steady state voltammogram was obtained, thereby increasing its stability and reproducibility.