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# Electrochemical synthesis of a novel purine-based polymer and its use for the simultaneous determination of dopamine, uric acid, xanthine and hypoxanthine

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ABSTRACT

A novel and simple electrochemical sensor based on the electro-polymerized film of 6-thioguanine (6-TG) modified on glassy carbon electrode (GCE) has been fabricated and used for the selective and simultaneous determination of dopamine (DA), uric acid (UA), xanthine (XA), and hypoxanthine (HXA) in 0.1 mol $L^{-1}$ phosphate buffer solution (PBS, pH 7.0) by using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. The results show that the polymerized 6-TG modified GCE (P6-TG/GCE) not only exhibits electrocatalytic effects toward electrochemical oxidations of DA, UA, XA and HXA with negatively shifted oxidation potentials and enhanced peak current responses, but also resolves the sluggish and overlapped voltammetric responses of DA, UA, XA and HXA into four strong and well-defined oxidation peaks using both CV and DPV, which can be applied for the selective and simultaneous determination of DA, UA, XA and HXA in their mixture. The surface morphology of the P6-TG film has been investigated by using a scanning electron microscope (SEM). The P6-TG film exhibits a nearly homogeneous surface structure with irregular and continuous holes and sticks standing on an electrode surface, which is helpful for the electrooxidations of analytes. Under the optimum conditions, the linear dependences of DPV current responses are observed for DA, UA, XA and HXA in the concentration ranges of 1–200 μmol $L^{-1}$, 2–1600 μmol $L^{-1}$, 1–500 μmol $L^{-1}$ and 2–800 μmol $L^{-1}$ with the correlation coefficients of 0.9986, 0.9997, 0.9997 and 0.9998, respectively. The detection limits are 0.05 μmol $L^{-1}$, 0.06 μmol $L^{-1}$, 0.30 μmol $L^{-1}$ and 0.10 μmol $L^{-1}$ for DA, UA, XA and HXA, respectively (S/N = 3). The different electrochemical behaviors of DA, UA, XA and HXA at various scan rates indicate that the electrode reaction of DA is an adsorption-controlled process, and those of UA, XA and HXA are diffusion-controlled processes at P6-TG/GCE. The application of P6-TG/GCE are demonstrated by simultaneously determining the concentrations of DA, UA, XA and HXA in human urine and serum samples by using standard adding method with satisfactory results.



## 1. Introduction

DA, UA, XA and HXA usually coexist in biological matrixes, and considered as the crucial molecules for some physiological processes in human metabolism. For instance, DA, widely distributed in cardiovascular, hormonal and central nervous systems for message transfer, plays a significant role in our body [1,2]; and abnormal DA levels will lead to Huntington's disease, tardive dyskinesia and neurodegenerative disorders, such as Parkinson's disease, HIV infection [2–4]. UA, XA and HXA are the degradation products of purine metabolism. The typical concentration of UA is 120–450 μmol $L^{-1}$ in blood and 1.4–4.4 mmol $L^{-1}$ in urine [5,6]; abnormal UA levels can cause several diseases, such as hyperuricemia, leukemia, and the Lesch–Nyhan syndrome [4,7]. The therapeutic XA level is 10–20 mg $mL^{-1}$ in blood [8], and the content of XA in blood plasma and urine may provide sensitive indicators of certain pathologic states, especially for xanthinuria. HXA is formed during the degradation of adenosine triphosphate [9], and found as a minor purine base in tRNA [8].

Just due to their importance for health, many methods have been studied for their analyses, such as high-performance liquid chromatography (HPLC) [10–12], capillary electrophoresis (CE) [13–15], enzymatic [16,17] and electrochemical [18–25] methods. Among these procedures, the enzyme-free electrochemical method is simple, rapid and low cost. Although many efforts have been paid to develop non-enzymatic electrodes, the selective and/or simultaneous determinations of DA, UA, XA and HXA at bare electrodes are nearly impossible because the oxidation potentials of DA and UA are very close, and also, the oxidation products adsorbed on electrode surfaces can lead to poor sensitivity and selectivity [26]. To overcome these obstacles, various materials have been used to modify the bare electrodes, such as conductive polymers [19,20], anodized nontronite [18], N-doped carbon microspheres [21], nanoparticles [22,26], carbon nanotubes [24,25], self-assembled monolayers [27], and metal oxides [28]. Unfortunately,

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most of the non-enzymatic sensors display drawbacks of high cost of rare metal precursors, low sensitivity and narrow linear ranges. So, the development of a simple, cheap, sensitive electrode for selective or simultaneous determination of DA, UA, XA and HXA is still demanded. Up to now, many studies have been reported for the simultaneous determination of DA and UA or UA, XA and HXA; while to our knowledge, there are few works for simultaneous determination of DA, UA, XA and HXA. Recently, X. Liu and co-workers fabricated a sensor based on the over-oxidized DA polymer and 3,4,9,10-perylenetetracarboxylic acid for simultaneous determination of ascorbic acid, DA, UA, XA and HXA [29]; Gong et al. reported the β-cyclodextrin modified GCE for simultaneous determination of UA, XA, HXA and DA [30].

Conjugated polymers derived from heterocyclic compounds have emerged as very promising materials for electronics, energy storage and conversion, electrochromic windows and sensors [4,31–33]. Thus, many conducting polymers, such as polythiophene [34,35], polyaniline [7,36,37], polypyrrole [38,39] and polythiazole [40,41] have received a great deal of interest; while, up to now, there is no study for simultaneous detection of DA, UA, XA and HXA by purine-based polymers.

In this work, a purine-based P6-TG film has been structured on a GCE surface via simple electropolymerization and used for selective and simultaneous determination of DA, UA, XA and HXA in 0.1 mol $L^{-1}$ PBS pH 7.0 by using CV and DPV (Scheme 1) techniques. The results show that P6-TG/GCE not only exhibits catalytic activities toward electro-oxidations of DA, UA, XA and HXA with negatively shifted oxidation over-potentials and enhanced peak current responses, but also resolves the sluggish and overlapped oxidation waves of DA, UA, XA and HXA into four strong and well-defined anodic peaks. Thus, the simultaneous detections of these species in human serum and urine samples have been investigated as real sample applications.

## 2. Materials and methods

### 2.1. Reagents and chemicals

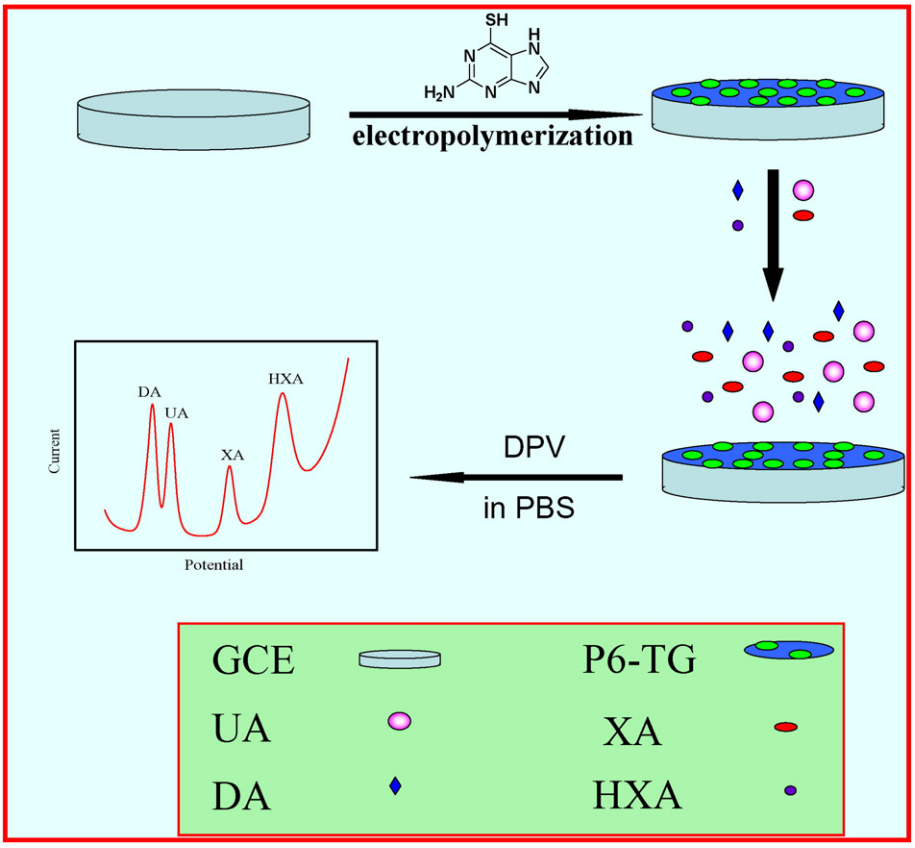
6-TG and HXA were purchased from Shanghai Meryer Chemical Technology (China), DA and UA were from Sigma (USA), XA was from Shanghai Dibo Chemical Factory (China). Phosphate buffer solutions (PBS, 0.1 mol $L^{-1}$) with various pH values were prepared using 0.1 mol $L^{-1}$ $Na_2HPO_4$, 0.1 mol $L^{-1}$ $NaH_2PO_4$ and 0.1 mol $L^{-1}$ KCl. Stock solutions of DA, UA, XA and HXA were freshly prepared as required in 0.1 mol $L^{-1}$ PBS pH 7.0. Distilled deionized water was used throughout the experiments. All other chemicals were of analytical grade and used without further purification.

### 2.2. Apparatus

All electrochemical experiments were performed with a CHI660C electrochemical workstation (Shanghai Chenhua). The conventional three-electrode system included a P6-TG modified GCE as working electrode, a saturated calomel as the reference electrode and a platinum wire as the auxiliary electrode.

DPV measurements employed a scan rate of 20 mV $s^{-1}$, a pulse amplitude of 25 mV, a pulse rate of 0.5 s, a pulse width of 60 ms and a quiet time of 2 s. For all the experiments, solutions and electrodes were motionless, solutions were deoxygenated by bubbling high purified nitrogen, and a nitrogen atmosphere was maintained over the solutions.

Electrochemical impedance spectra (EIS) were obtained in the presence of a 1 mmol $L^{-1}$ $K_3Fe(CN)_6$ + 1 mmol $L^{-1}$ $K_4Fe(CN)_6$ + 0.1 mol $L^{-1}$ 1 $KNO_3$ solution, using an alternating current voltage of 5 mV. Impedance measurements were carried out at an open circuit potential of 0.18 V in a frequency ranging from 0.01 to 100,000 Hz. An S-4800




**Scheme 1.** Schematic representation of the simultaneous electro-catalytic oxidation of DA, UA, XA and HXA at P6-TG/GCE.